

UNCLASSIFIED

AD _____

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION ALEXANDRIA, VIRGINIA

DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DCD DIR 5200.10



UNCLASSIFIED

THIS REPORT HAS BEEN DECLASSIFIED
AND CLEARED FOR PUBLIC RELEASE.

DISTRIBUTION A
APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

AD No. 9292
ASTIA FILE COPY

QUARTERLY PROGRESS REPORT

APRIL 15, 1953

SOLID-STATE AND MOLECULAR THEORY GROUP
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

AD-9292

QUARTERLY PROGRESS REPORT NO. 8

SOLID-STATE AND MOLECULAR THEORY GROUP

Massachusetts Institute of Technology
Cambridge, Massachusetts

O. N. R. Contract N5ori-07856

April 15, 1953

PERSONNEL

Faculty

Professor J. C. Slater, Director

Professor P. M. Morse

Research Assistants and Staff Members

L. C. Allen

E. R. Callen

F. J. Corbató (In Professor Morse's group)

A. J. Freeman

H. Kaplan

R. Kikuchi

H. Statz

H. C. White

Research Fellow

J. H. Barrett

Fellow in Chemistry

R. E. Merrifield

Staff Members, Lincoln Laboratory (Air Force Contract No. AF 19(122)-458)

W. H. Kleiner

G. F. Koster

A. Meckler

R. H. Parmenter

G. W. Pratt, Jr.

H. C. Schweinler

Secretary

Phyllis E. Fletcher

TABLE OF CONTENTS

Survey	1
1. A Two-Electron Example of Ferromagnetism, J. C. Slater	6
2. A Simple Model of Ferromagnetism, H. Statz	20
3. Theory of Ferromagnetism, R. Kikuchi	21
4. A Spin Operator Method, G. W. Pratt, Jr.	23
5. The Water Molecule, G. F. Koster, H. C. Schweinler	46
6. Spherical Bessel Functions of Half Integral Order and Imaginary Argument, F. J. Corbató, G. F. Koster, H. C. Schweinler	48
7. Configuration Interaction Applied to the Hydrogen Molecule, E. Callen	49
8. Nuclear Electric Quadrupole Interaction in the KCl Molecule, L. C. Allen	51
9. Configuration Interaction in the Hydrogen Fluoride Molecule, R. E. Merrifield	52
10. Configuration Interaction for the Fluorine Molecule, J. H. Barrett	53
11. The Carbon -- Carbon Bond in Ethane, A. Meckler	55
12. Limited Configuration Interaction Treatment of the NH_3 Molecule, H. Kaplan	57
13. A Study of $2Z_p$ in Atoms, A. J. Freeman	59
14. Orbital Effect in Neutron-Electron Magnetic Scattering, W. H. Kleiner	61
15. Adsorbed Surface Layers on Semiconductors, H. Statz	64
16. Connection Between the Many-Electron Interaction and the One-Electron Periodic Potential Problems, H. C. White	65

Quarterly Progress Report No. 8

on

Project N5ori-07856

SURVEY

The progress of the Group in the preceding three months is only partly summarized in this Quarterly Progress Report, for the reason that much thought on the part of almost everyone has gone into general problems of molecular theory, which I have been presenting in the advanced course mentioned in the preceding Quarterly Progress Report. As I mentioned there, the notes of that course are being prepared as Technical Report No. 3 of the Solid-State and Molecular Theory Group, entitled, "Electronic Structure of Atoms and Molecules", and dated February 15, 1953. This Technical Report will go to the same distribution list as these Quarterly Progress Reports, and presumably will have reached its readers before this Report appears. Many members of the Group have made extremely valuable contributions to the preparation of the Technical Report, which do not appear in the present Report; in particular, I should like to thank Dr. Koster, whose help with the application of group theory to the configuration interaction problem in molecules, particularly in methane, has been of great value.

This course on atoms and molecules will be followed during the second half year with one on the structure of solids, and its notes are being written up in the same way, so that Technical Report No. 4, on "Electronic Structure of Solids", will appear sometime after the close of the term in June. The general background which has been built up in the discussion of molecules will be carried over to the problem of solids. That is, in the first part of the course we shall consider one-electron solutions in a self-consistent field, and in the second part shall set up determinantal solutions formed from these one-electron orbitals, and consider the problem of configuration interaction between them. In considering the symmetry, both of one-electron orbitals and of the wave functions of the complete system, we shall be concerned not only with the translational symmetry arising from the crystalline nature of the problem, but with rotation and reflection symmetry as well; it is for this reason that we carried through the long discussion of molecules, which show only the rotation and reflection symmetry without the translational symmetry. We shall propose to discuss symmetry properties of energy bands and Wannier functions, degeneracy of energy bands, and so on, making use as during the first term of only the minimum amount of group theory to lead to the desired results. In the study of configuration interaction, major emphasis will be placed on magnetic problems, excitons, and similar questions.

During the preceding three months, the Group has gone ahead with the general lines of research discussed in the preceding Progress Report. The major efforts have concerned ferromagnetism and antiferromagnetism on the one hand, molecular structure on the other. In the preceding Progress Report, Dr. Statz in his contribution, and I in the Survey, pointed out the interest of the problem of the interaction of two electrons in an empty band, or two

(SURVEY)

electrons in an empty band, or two holes in an otherwise filled band, and showed that these would tend to set themselves with antiparallel spins if the band were not degenerate, but that if it were degenerate, like the d band in a ferromagnetic metal, they could well tend to set themselves with parallel spins. suggesting that further electrons or holes would also line up, and lead to ferromagnetism. The energy difference between the parallel and antiparallel orientation depended on an intra-atomic exchange integral, the same one leading to Hund's rule in an isolated atom. This did not, however, indicate an energy difference, or ferromagnetic interaction, which remained finite at infinite internuclear separation, for this integral must be multiplied by a factor measuring the probability of finding the two electrons or holes on the same atom, and this factor goes to zero in the limit of infinite nuclear separation, since it measures the probability of finding an ionic state, whereas the actual ground state is strictly non-ionic at infinite distance. In other words, the correlation effect, which keeps electrons out of each other's way increasingly as the atoms get far apart, cancels the intra-atomic exchange effect at great enough distances.

We have now carried this argument a good deal further, and can present it with much more mathematical rigor, as I show in my contribution to the present Progress Report. The theory in this form is being written up for publication by the writer, Statz, and Koster. A one-dimensional model which shows the main physical features of the real problem can be solved exactly, and we see straightforwardly the way in which the correlation effect comes in. We are still dealing with only two electrons, or two holes, but the arguments seem so general that the writer feels that we are just about ready to apply concepts which we have worked out for this two-electron case to setting up a general semi-quantitative theory of ferromagnetism, which should supplant both the Heisenberg and the naive energy-band or collective electron theories, and take proper account of configuration interaction and its relation to the correlation energy.

Dr. Statz makes a further contribution to the theory of overlapping bands in the present Report, and Dr. Kikuchi carries further the model which he reported on in the preceding Report. This model, as we now see, probably does not actually correspond to ferromagnetism, but it seems worthwhile to carry its discussion through.

While we feel that our knowledge of ferromagnetism is advancing rapidly, the problem of antiferromagnetism is much more difficult. Dr. Pratt became convinced that the simplified one-dimensional model which he was using earlier would not lead to antiferromagnetism, and we are now looking for a model much closer to the actual substances known to be antiferromagnetic. We feel, as do most of the workers in the field, that the oxygen in such an antiferromagnetic substance as MnO undoubtedly plays a very important role, and that a linear molecule $(\text{MnOMn})^{++}$ would presumably show antiferromagnetic properties. It thus seems extremely interesting to investigate the energy levels of such a molecule properly, and Dr. Pratt is starting such an investigation. The complete configuration interaction problem would be prohibitively difficult, but it seems possible to carry out a treatment which should

(SURVEY)

give the required result, without impossible labor. We shall confine ourselves to the case where all five spins of the 3d electrons in each Mn^{++} ion are lined up parallel, but where the magnetic moments of the two Mn^{++} ions can have various relative orientations, all the way from parallel (ferromagnetic configuration) to antiparallel (antiferromagnetic). In other words, we must find the relative energies of the configurations with different total spins. We are considering not only the case where each Mn ion is doubly charged, and where the oxygen forms an $O^{=}$ ion with an inert gas configuration, but also the case where the oxygen has lost one of these electrons, which is then located on one of the Mn ions, reducing its total magnetization. This, in other words, is the model which has been discussed by Anderson and others from the point of view of superexchange, but instead of treating it by the Heitler-London method, we propose to treat the same model quantitatively by the configuration interaction method, using properly orthogonalized molecular orbitals.

This problem of configuration interaction, even making the approximations which we have mentioned, still is exceedingly difficult to carry out, not on account of the number of interacting configurations, which is not very large, but on account of the problem of setting up the correct unperturbed functions to represent the various orientations of the Mn ions in their states of maximum multiplicity, and the wave functions of the molecule arising from them. These wave functions are linear combinations of very large numbers of determinantal functions formed from one-electron orbitals. In studying this problem, Dr. Pratt has been led to treat the problem of spin degeneracy in a new and greatly improved way, which is the subject of his communication. Some such technique as this is absolutely necessary to handle the complication of the $MnOMn$ problem, and at the same time it should lead to a great improvement in our ability to handle the problem of spin degeneracy in general, which comes up in almost all molecular and solid-state problems. For instance, the case of the 14 singlets arising from the spin degeneracy of 8 electrons, which Dr. Pratt discusses as a simple example in his paper, represents the most complicated case which has been worked out, with great difficulty, by previous methods.

The molecular calculations are all in a very early stage, and some changes in program have been made since the preceding Progress Report. Drs. Koster and Schweinler are going on with the work on water, but this will be a task requiring a good many months. Since the preceding Progress Report, it has appeared that other work which has been carried out very recently elsewhere on the spherical Bessel functions, which are needed for the calculation of three-center integrals, will make it unnecessary to compute those functions here, so that that part of the program has been discontinued. Mr. Merrifield is proceeding with the work on HF, preliminary to studying $(FHF)^-$, but it now appears that the HF case will represent a large enough task for the present, and he will not go ahead with the $(FHF)^-$ case. It is hoped that this problem will be taken over by another member of the Group. Dr. Barrett has started work on F_2 , a problem which makes use of the same atomic wave functions. Mr. Allen continues his study of KCl, with particular attention to the polarization, and Mr. Callen

(SURVEY)

is going ahead with the study of the configuration interaction approach to the hydrogen molecule.

It is becoming clearer and clearer that while a complete treatment of configuration interaction is a very desirable thing, the number of interacting configurations will be so great, in many cases even of simple molecules, that a complete treatment will be quite out of the question. Thus, in my Technical Report No. 3, it is shown that a proper treatment of configuration interaction in methane, of approximately the same degree of accuracy as that used by Meckler for oxygen, would require 104 interacting configurations, a number much greater than has been suspected by earlier writers on the subject. This is clearly out of the question, and our attention is turning more and more to possible methods of simplifying the configuration interaction problem by leaving out unimportant configurations. In my Technical Report, I have suggested several possible ways of doing this, none of which can be really justified except by trying them out. One is a possible treatment of the carbon-carbon bond in ethane, by which enough configurations would be included so that the carbon-carbon bond itself would have a wave function which behaved properly as a function of C-C distance, but in which the hydrogens were treated only to a molecular orbital approximation. This would imply that the problem was set up in terms of some sort of directed orbitals, that the two electrons in the bond between a carbon and a hydrogen were located in the bonding orbital formed from these directed orbitals, but that the two electrons in the carbon-carbon bond were either both in the bonding, or both in the antibonding, type of molecular orbital. Such an interaction, which involves only two configurations, leads to proper behavior of the two methyl radicals into which the molecule dissociates. Dr. Meckler, who has now submitted his paper on oxygen for publication, is starting this treatment of ethane, hoping in this way to get a treatment of the carbon-carbon bond which may point the way to methods of investigating a single bond fairly accurately, without having to solve the complete configuration problem of the whole molecule.

Such a treatment of a single bond suggests that by using directed orbitals, one may perhaps be led to a simpler configuration interaction than the whole general case. For instance, in my Technical Report, I have shown that in methane one can proceed by setting up bonding and antibonding directed orbitals between the carbon and the various hydrogens. One can then set up those particular configurations in which two electrons are located on each of the four bonds. It is plausible that these may be more important configurations, for the actual internuclear distance, than those in which some bonds have more, some less, than two electrons. It appears that there are only 22 configurations of this type, out of the whole 104 of the molecule. These configurations would not lead to the correct state of the carbon atom at infinite internuclear distance, but would instead leave it in its so-called valence state, but nevertheless such a treatment might be good enough to be of considerable value. A similar treatment of ammonia involves only 13 configurations, out of a total of 98, and Dr. Kaplan has decided to undertake this problem, in place of S_8 which he originally proposed to consider.

(SURVEY)

The number of interacting configurations in S_0 is so enormous that nothing but a simple molecular orbital treatment would be possible, whereas with ammonia we should be able to use this limited configuration interaction treatment.

It is clear that in these limited applications of configuration interaction we are feeling our way toward approximations which may be usable and yet good enough to be valuable in more complicated cases. In particular, for solids, any complete configuration interaction problem is absurd to think about, unless we can limit it either by limiting the number of electrons out of closed shells, as in the case of the ferromagnetic model discussed by Statz and the writer, or by some method which focuses our attention on a particular bond or particular atom and its immediate environment. Configuration interaction proves to be very important in those molecular problems where it can really be treated properly, and there is no reason to think that it is not equally important in solids. Thus the sort of study which we are making is the only approach which seems to us at all reliable, to the question of how it can be handled for solids in a practicable way.

A number of other problems are being carried along. Mr. Freeman has completed his study of the Z_p 's for atoms, as determined by the Hartree method, and is preparing to write this up. Dr. Kleiner has finished one phase of his study of neutron scattering, and has sent a Letter to the Editor of The Physical Review concerning it. Dr. Parmenter has finally abandoned the attempt to set up the energy bands in chromium, on account of the enormous number of three-center integrals involved. Mr. White continues his study of the many-electron interaction by the method of Tomonaga.

Several new students, both seniors and graduate students, are joining the group. Mr. Schrieffer and Mr. Switendick, seniors, are writing senior theses on problems of atomic complex spectra, working out the multiplet separations of light atoms from simple analytic wave functions. Mr. Saffren, and other graduate students, are starting to collaborate with various members of the Group, and will be reporting progress at a later time. The plans for next year, when some of these new students will be with the Group, as well as various visitors from overseas and other places, indicate that there will be a large and very active group during the year.

J. C. Slater

1. A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM

In the preceding Quarterly Progress Report, H. Statz⁽¹⁾ has discussed a simple case of ferromagnetism: that in which there are only two electrons in an empty band, or two holes in a filled band, the extension to the latter case having been supplied by G. F. Koster.⁽²⁾ The question was asked, will the lowest state of this system correspond to the electrons having parallel spin (a triplet state), in which case we expect it to form a model for ferromagnetism, or to their having antiparallel spin (a singlet), in which case the system would not be ferromagnetic? The answer was straightforward in case the band was non-degenerate: the singlet will lie lower, and the system will be non-magnetic. In the case of degenerate bands, it was shown that the triplet state could well lie lower, so that the system would be ferromagnetic. The analysis underlying these conclusions has now been carried further, and put on a sounder basis, and will be presented here. The conclusions are the same as before, but particularly in the case of overlapping bands and ferromagnetism, we get a clearer and more detailed understanding of the situation. The work is now being written up for publication.

As in Ref. 1, the wave function for the two-electron system is expanded in sums of products of Wannier functions. Let the Wannier function corresponding to the i^{th} energy band, concentrated around the atom whose vector position is at \vec{R}_m , to be $a_i(\vec{r} - \vec{R}_m)$. These Wannier functions form a complete orthogonal set, provided we use all bands i , and all atomic positions \vec{R}_m . The function $\psi(\vec{r}_1, \vec{r}_2)$ of the coordinates of the two electrons, satisfying Schrodinger's equation, can then be expanded in the form

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{i, j, m, n} U_{ij}(\vec{R}_m, \vec{R}_n) a_i(\vec{r}_1 - \vec{R}_m) a_j(\vec{r}_2 - \vec{R}_n). \quad (1.1)$$

This equation is similar to Eqs. (10.5) and (10.10) of Ref. 1. Here, however, in contrast to the treatment of Ref. 1, we handle the symmetry or antisymmetry of the wave function by making appropriate postulates about the symmetry of $U_{ij}(\vec{R}_m, \vec{R}_n)$. The function (1.1) does not include the spin, and we know, from general treatment of the two-electron problem, that it must be a symmetric function of the coordinates \vec{r}_1, \vec{r}_2 for a singlet, an antisymmetric function for a triplet. These conditions are fulfilled if the U_{ij} 's satisfy the condition

$$U_{ji}(\vec{R}_n, \vec{R}_m) = \pm U_{ij}(\vec{R}_m, \vec{R}_n), \quad (1.2)$$

where the $+$ sign refers to the singlet, the $-$ to the triplet.

We now assume, as in Ref. 1, that the Hamiltonian is given by

$$H = H_1 + H_2 + g_{12} \quad (1.3)$$

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

where H_1 , H_2 are one-electron Hamiltonians of the two electrons in a periodic crystalline field, and where g_{12} is the Coulomb repulsion between the two electrons (or holes). We assume that the energy of an electron in the field given by the Hamiltonian H_1 , in the i^{th} energy band, with a propagation constant \vec{k} , is given by

$$\sum_m \mathcal{O}_i(\vec{R}_m) \exp(-i\vec{k} \cdot \vec{R}_m). \quad (1.4)$$

Then the matrix components of H_1 between the various Wannier functions are

$$\int a_i^*(\vec{r}_1) H_1 a_j(\vec{r}_1 - \vec{R}_m) d\tau_1 = \delta_{ij} \mathcal{O}_i(-\vec{R}_m). \quad (1.5)$$

We can now find the matrix components of the Hamiltonian (1.3) between the various products of Wannier functions included in (1.1), and thus set up the general equations for the U_{ij} 's, similar to Eq. (10.7) of Ref. 1. These equations are

$$\begin{aligned} \sum_s [\mathcal{O}_i(\vec{R}_s) U_{ij}(\vec{R}_m - \vec{R}_s, \vec{R}_n) + \mathcal{O}_j(\vec{R}_s) U_{ij}(\vec{R}_m, \vec{R}_n - \vec{R}_s)] + \sum_{k,l,r,s} U_{kl}(\vec{R}_m - \vec{R}_r, \vec{R}_n - \vec{R}_s) \\ \int a_i^*(\vec{r}_1 - \vec{R}_m) a_j^*(\vec{r}_2 - \vec{R}_n) g_{12} a_k(\vec{r}_1 - \vec{R}_m + \vec{R}_r) a_l(\vec{r}_2 - \vec{R}_n + \vec{R}_s) d\tau_1 d\tau_2 \\ = EU_{ij}(\vec{R}_m, \vec{R}_n). \end{aligned} \quad (1.6)$$

In Eq. (1.6), we can now carry out a separation of variables into the coordinates of the center of mass of the two electrons, and the relative coordinates. This separation is equivalent to making use of the conservation of momentum: if we set up our function ψ , not in terms of the Wannier functions as in Eq. (1.1), but in terms of Bloch functions, the sum of the \vec{k} vectors of the two electrons will form a quantity which is conserved, only those states interacting with each other for which this sum has a fixed value. The corresponding statement regarding the U 's is that we may write

$$U_{ij}(\vec{R}_m, \vec{R}_n) = \exp(i\vec{K} \cdot (\vec{R}_m + \vec{R}_n)) F_{ij}(\vec{R}_m - \vec{R}_n), \quad (1.7)$$

where the exponential factor represents the free motion of the center of mass, \vec{K} being a momentum vector associated with this free motion, and where $F_{ij}(\vec{R}_m - \vec{R}_n)$ represents the relative motion, depending only on $\vec{R}_m - \vec{R}_n$, the distance between the particles. If we substitute (1.7) in Eq. (1.6), and replace $\vec{R}_m - \vec{R}_n$ by a single quantity \vec{R}_p , the resulting equation reduces to

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

$$\begin{aligned} & \sum_s \left[\mathcal{O}_i(\vec{R}_s) \exp(-i\vec{K} \cdot \vec{R}_s) F_{ij}(\vec{R}_p - \vec{R}_s) + \mathcal{O}_j(\vec{R}_s) \exp(-i\vec{K} \cdot \vec{R}_s) F_{ij}(\vec{R}_p + \vec{R}_s) \right] \\ & + \sum_{k,l,i,s} \exp(-i\vec{K} \cdot (\vec{R}_r + \vec{R}_s)) F_{kl}(\vec{R}_p - \vec{R}_r + \vec{R}_s) \int a_i^*(\vec{r}_1 - \vec{R}_p) a_j^*(\vec{r}_2) g_{12} \\ & a_k(\vec{r}_1 - \vec{R}_p + \vec{R}_r) a_l(\vec{r}_2 + \vec{R}_s) d\tau_1 d\tau_2 = E F_{ij}(\vec{R}_p). \end{aligned} \quad (1.8)$$

We are interested in solving these equations for a particular value of \vec{K} . Usually the lowest state, which we are interested in, will correspond to $\vec{K} = 0$, and we shall assume that this is the case in our further discussion. We may then investigate the wave function relating to the relative coordinates, from (1.8). We readily find that the quantity $F_{ij}(\vec{R}_p)$ has symmetry properties similar to those given in Eq. (1.2):

$$F_{ji}(-\vec{R}_p) = \pm F_{ij}(\vec{R}_p). \quad (1.9)$$

For the coefficients $F_{ii}(\vec{R}_p)$ associated with the case where both electrons are in the same band, Eq. (1.9) means that $F_{ii}(\vec{R}_p)$ must be an even function of \vec{R}_p (that is, even under an inversion operation) for a singlet, odd for a triplet, as in Ref. 1, and this immediately leads to the conclusion that $F_{ii}(0) = 0$ for a triplet. For the case where i and j are different in Eq. (1.9), however, we have the possibility of writing F_{ji} in terms of F_{ij} , and when we do so, we arrive at equations equivalent to Eq. (10.11) of Ref. 1.

We now wish to take simplified cases of Eq. (1.8), which are simple enough so that we can solve them, and yet which are general enough so that they preserve the important physical features of the general equations. In the first place, as was shown in Ref. 1, the largest integrals of the operator g_{12} in Eq. (1.8) come when all four Wannier functions are on the same atom. For the present approximate survey, we shall consider only these terms, disregarding all others, though those others would have to be taken into account to get a quantitatively accurate solution. We shall use the abbreviation

$$\int a_i^*(\vec{r}_1) a_j^*(\vec{r}_2) g_{12} a_k(\vec{r}_1) a_l(\vec{r}_2) d\tau_1 d\tau_2 = (ij/g/kl). \quad (1.10)$$

Then, for the case $\vec{K} = 0$, Eq. (1.8) reduces to the form

$$\sum_s \left[\mathcal{O}_i(\vec{R}_s) + \mathcal{O}_j(-\vec{R}_s) \right] F_{ij}(\vec{R}_p - \vec{R}_s) + \delta(\vec{R}_p, 0) \sum_{k,l} (ij/g/kl) F_{kl}(\vec{R}_p) = E F_{ij}(\vec{R}_p), \quad (1.11)$$

where in the second term of the first summation we have replaced \vec{R}_s by $-\vec{R}_s$. We shall now

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

consider two cases of Eq. (1.11): first that in which only one energy band is of importance, so that all the F_{ij} 's can be disregarded unless i and j are both equal to a , the index of this band; secondly, that in which two bands, a and b , must be considered, so that we consider all cases where either i or j equals either a or b .

We take first the case of one band, so that $i = j = a$. We note that the energy $\mathcal{E}_a(\vec{R}_s)$ must be symmetrical under an inversion, so that $\mathcal{E}_a(\vec{R}_s) = \mathcal{E}_a(-\vec{R}_s)$. Then Eq. (1.11) reduces to

$$\sum_s 2 \mathcal{E}_a(\vec{R}_s) F_{aa}(\vec{R}_p - \vec{R}_s) + (aa/g/aa) F_{aa}(\vec{R}_p) \delta(\vec{R}_p, 0) = E F_{aa}(\vec{R}_p), \quad (1.12)$$

where we remember that for the singlet the function $F_{aa}(\vec{R}_p)$ is even under an inversion, while for a triplet it is odd. The term $(aa/g/aa)$ represents the repulsive interaction between the two electrons, which we are neglecting unless they are on the same atom, so that the relative separation \vec{R}_p reduces to zero. For the triplets, this term drops out entirely, since $F_{aa}(0) = 0$ for the triplets, and the equations are exactly as they would be for free particles. For the singlets, however, the repulsive interaction is present, and tends to keep the two electrons apart. Thus this repulsive interaction will tend to raise the energy of all singlet states, while leaving the triplets unchanged, and we must first examine whether it can raise the energy of the lowest state, which as shown in Ref. 1 is a singlet, up to the next lowest, which is a triplet.

We shall discuss this problem directly from the difference equations (1.12). A three-dimensional difference equation of this type cannot be easily solved; the relaxation method, used for the approximate solution of two- and three-dimensional differential equations when approximated by difference equations, is probably the best method of handling it. The one-dimensional case, however, is easy to treat, and as shown in Ref. 1, this shows all the essential features of the three-dimensional problem. Even the one-dimensional case is rather complicated if we have interactions between other than nearest neighbors; that is, if $\mathcal{E}_a(\vec{R}_s)$ is appreciable except for \vec{R}_s equal to the distance between nearest neighbors. We recall, from Eq. (1.4), that a restriction to nearest neighbor interactions is another way of saying that the energy is a sinusoidal function of k , the propagation vector, an approximation which holds well for narrow bands. We shall then set up the special case of Eq. (1.12) in which \vec{R}_p is restricted to an equally spaced set of points on a line, and \vec{R}_s refers only to a unit displacement. Essentially this same problem was discussed by the writer and Shockley⁽³⁾ in treating the similar problem of the exciton.

To simplify notation, let the various lattice points be denoted by an index n . Here $n = 0$ refers to $\vec{R}_p = 0$, positive and negative values of n to positive and negative \vec{R}_p 's (that is, to the case where the first particle is to the right or left of the second), and in accordance with the discussion of Ref. 1, we shall impose the boundary condition that our function is to

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

vanish for given limits of \vec{R}_p , or of the relative coordinates; in particular, we assume that the function will vanish for $n = \pm N$. Let the one non-vanishing component of \mathcal{C}_a be simply denoted as \mathcal{C}_a . Let the F_{aa} 's be denoted by $F_{aa}(n)$. Then Eq. (1.12) becomes

$$\begin{aligned} 2 \mathcal{C}_a [F_{aa}(n+1) + F_{aa}(n-1)] &= E F_{aa}(n) \text{ if } n \neq 0 \\ 2 \mathcal{C}_a [F_{aa}(1) + F_{aa}(-1)] + (aa/g/aa) F_{aa}(0) &= E F_{aa}(0) \end{aligned} \quad (1.13)$$

We can at once solve all of Eqs. (1.13) except that for $n = 0$ by the assumption

$$\begin{aligned} F_{aa}(n) &= \sin(N-n) \text{ if } 0 \leq n \leq N \\ F_{aa}(-n) &= \pm F_{aa}(n), \end{aligned} \quad (1.14)$$

where the \pm sign refers to singlets or triplets. The solution (1.14) is chosen so that it automatically satisfies the boundary conditions when $n = \pm N$. Substitution of (1.14) in the first equation of (1.13) shows that that equation is satisfied if

$$E = 4 \mathcal{C}_a \cos \alpha. \quad (1.15)$$

which is what we expect from Eq. (1.4), when we remember that we are dealing with the energy of two electrons. We note, incidentally, that to have the energy a minimum for $\alpha = 0$ (or for $k = 0$ in Eq. (1.4)), which is the convenient assumption to make, \mathcal{C}_a must be negative.

We must now substitute in Eq. (1.13) for $n = 0$, to determine the propagation constant α , and hence the energy of each state. For the triplet states, this is trivial. We must have $F_{aa}(0) = 0$, which demands at once $\sin \alpha N = 0$, $\alpha = m\pi/N$, where $m = 1, 2, \dots, N-1$, so that we have $N-1$ triplet states. For the singlets, we have $-4 \mathcal{C}_a \cos \alpha N \sin \alpha + (aa/g/aa) \sin \alpha N = 0$, or

$$4 \mathcal{C}_a \cot \alpha N \sin \alpha = (aa/g/aa). \quad (1.16)$$

We can solve this transcendental equation by plotting the quantity $-\cot \alpha N \sin \alpha$ as a function of α , and finding the values of α for which it equals $-(aa/g/aa)/4 \mathcal{C}_a$, which we remember is a positive quantity, since \mathcal{C}_a is chosen to be negative. In Fig. 1-1 we show the function $-\cot \alpha N \sin \alpha$, as a function of α , for $N = 4$. At $\alpha = 0$ the function equals $-1/N$. It goes through zero when $\alpha N = \pi/2, 3\pi/2, \dots$, or in general for $\alpha = m\pi/2N$ where m is an odd integer, so that it goes through zero N times for α between zero and π . At $\alpha = \pi$, the function equals

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

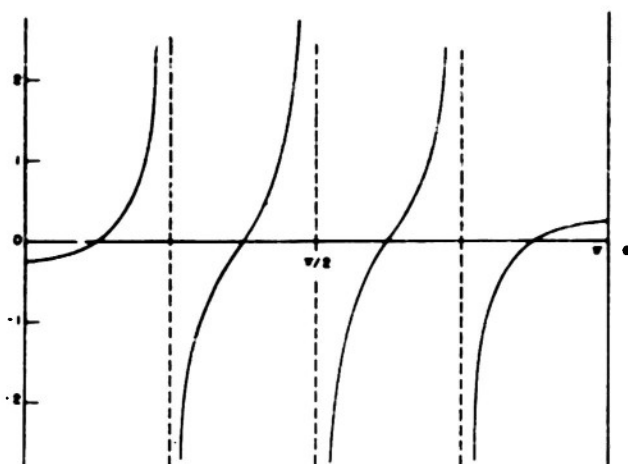


Fig. 1-1

Function- $\cos aN \sin a$, for $N = 4$

$1/N$. The function becomes infinite when $a = m\pi/N$ where m is any integer from 1 to $N - 1$; that is, it becomes infinite at the same values of a for which we have triplet states.

We now see that if $(aa/g/aa) = 0$, so that we have the problem of the free particles, we have N singlet states, corresponding to the values of a where this curve is zero. The lowest singlet state, corresponding to $a = \pi/2N$, is the lowest state of the problem, below the lowest triplet, which has $a = \pi/N$, as is discussed in Ref. 1. To visualize the energies, we remember that the energy is given by $4 \mathcal{E}_a \cos a$, where \mathcal{E}_a is negative, so that $a = 0$ corresponds to the center of the Brillouin zone, $a = \pm \pi$, to its edges, and the energy has its minimum at the center of the zone, its maximum at the edges. Thus increasing a increases the energy. Now as $(aa/g/aa)$ increases from zero, or as the repulsive effect between electrons is introduced, we find the singlet values of a from Fig. 1-1 by finding the intersections of the curve with the horizontal line at height $-(aa/g/aa)/4 \mathcal{E}_a$, depending on the magnitude of the repulsive interaction in terms of the band width. As this line rises, it is clear that the a 's of all singlet levels increase, so that their energies rise, a consequence of the positive repulsive energy. These a 's, however, approach the asymptotic values which give the triplet energies, as the repulsive interaction is indefinitely increased; so that no matter how great the repulsion, or how narrow the band width, the lowest singlet will never rise above the lowest triplet. This is in agreement with the result of Ref. 1.

For small values of $(aa/g/aa)$, there are N intersections of a horizontal line with the curve of Fig. 1-1. That is, there are N singlet states, and taken together with the $N - 1$ triplets, we have $2N - 1$ states in all, which is as it must be, since there are $2N - 1$ values of n , between $n = -N$ and $+N$, for each of which a quantity $F_{aa}(n)$ is defined, and there must be as many states as values of this quantity. At a certain height, however, the intersection in Fig. 1-1 corresponding to the largest a value becomes lost, and we must investigate what happens to this solution, though it is not the one that concerns us directly, since it corresponds

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

to the highest singlet, and we are principally interested in the lowest singlet. It is interesting first to see for what value of $(aa/g/aa)$ this occurs. From what we have seen before, it comes when $-(aa/g/aa)/4 \mathcal{E}_a = 1/N$. This has a simple meaning. The quantity $-4 \mathcal{E}_a/N$ is the total band width, $-8 \mathcal{E}_a$, divided by $2N$, the number of lattice points plus one, or is approximately the one-electron energy per lattice point at the top of the energy band. Our limiting condition comes when the repulsive interaction $(aa/g/aa)$ equals this band energy per lattice point. We shall now show that for larger values of $(aa/g/aa)$, this solution emerges from the top of the band, and becomes a higher and isolated energy level, equal in energy approximately to $(aa/g/aa)$ in the limit of very high repulsive energy, and corresponding to a wave function in which the two electrons are attached permanently to the same atom, never wandering through the lattice. This special solution can be at once identified from Eq. (1.13). In case $(aa/g/aa)$ is very large compared to \mathcal{E}_a , we can almost disregard \mathcal{E}_a in Eq. (1.13). Then we have a limiting solution in which $F_{aa}(n) = 0$ except for $n = 0$, in which case of course $F_{aa}(0)$ must be unity by normalization (it is to be noticed that we have not so far normalized our wave functions). Eq. (1.13) then tells us that $E = (aa/g/aa)$.

The physical meaning of this special solution is clear. In the limit of narrow bands, where \mathcal{E}_a is negligible, Eq. (1.13) leads to no non-diagonal matrix components, which means that electrons are not likely to wander from one atom to another. In our problem of the relative motion of the electrons, there is one lattice point, $R_p = 0$ or $n = 0$, corresponding to an ionic state; all the remaining $2N - 2$ lattice points correspond to non-ionic states, with the two electrons on different atoms. These $2N - 2$ states will be degenerate with each other, and as soon as the non-diagonal matrix components \mathcal{E}_a become different from zero, linear combinations will be introduced corresponding to the wandering of electrons from one lattice point to another to remove this degeneracy. The one ionic state, however, will have a much higher energy, and it will remain as an isolated state until the \mathcal{E}_a 's become great enough so that there is an appreciable probability of mixing ionic states with the non-ionic ones arising from the $2N - 2$ remaining states.

The importance of this special ionic state arises from its effect on the other states in the limit of narrow bands. If our wave functions are all normalized, then the completeness theorem demands that the sum of the squares of the $F_{aa}(n)$'s, for a given n , for all the states in the band, must equal unity. We have just seen that in the limit of narrow bands, the single ionic state will have $F_{aa}(0)$ equal approximately to unity, so that this means that in this limit, all the other states must have $F_{aa}(0)$ approximately zero. In other words, all the states, singlets as well as triplets, must lead to a vanishing probability of ionic arrangements of two electrons on the same atom, in the limit of narrow bands, or infinite internuclear distance. This is the origin of the correlation effect, tending to keep electrons from occupying the same atom in the limit of widely separated atoms. We can investigate this correlation effect directly, through our exact solution for $F_{aa}(0)$ for the various states, and we shall do this presently. But it is very important that we can deduce the correlation effect as well by use of the com-

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

pleteness theorem, for this can be used in the three-dimensional case, where we cannot get an exact solution of the difference equations, just as well as in this soluble one-dimensional case. The completeness relation holds equally well there, and inspection of the difference equation will show that this special ionic state occurs perfectly generally, and is not limited to the one-dimensional problem.

Let us now see analytically how these results come about. First we shall investigate the ionic state, when $(aa/g/aa)$ is great enough so that it no longer can be described in terms of the solution we have set up already. In this case, we easily find that the substitute for Eq. (1.14) is

$$\begin{aligned} F_{aa}(n) &= (-1)^n \sinh \gamma(N - n), \\ F_{aa}(-n) &= F_{aa}(n), \end{aligned} \quad (1.17)$$

where we use only the + sign in the relation between $F_{aa}(-n)$ and $F_{aa}(n)$, since this special solution occurs only for the singlets. The energy equation, corresponding to (1.15), is then

$$E = -4 \mathcal{E}_a \cosh \gamma. \quad (1.18)$$

When we substitute in the equation for $n = 0$, to determine the value of γ , we find

$$-4 \mathcal{E}_a \coth \gamma N \sinh \gamma = (aa/g/aa). \quad (1.19)$$

We may plot $\coth \gamma N \sinh \gamma$ as a function of γ , in a way similar to Fig. 1-1, to determine the value of γ graphically. When $\gamma = 0$, $\coth \gamma N \sinh \gamma$ equals $1/N$, so that the limiting case $-(aa/g/aa)/4 \mathcal{E}_a = 1/N$ corresponds to $\gamma = 0$, just as it corresponds to $a = \pi$. As $(aa/g/aa)$ increases from this value, γ increases without limit. If N is large, the quantity $\coth \gamma N$ very rapidly approaches unity, so that Eq. (1.19) can be solved directly. For large γ , Eq. (1.17) shows that $F_{aa}(n)$ decreases very rapidly with increasing n , so that $F_{aa}(0)$ is much larger than any of the other values. This verifies our earlier statement that this state is one in which practically the entire function is concentrated at $\vec{R}_p = 0$, corresponding to the ionic state. Furthermore, for large γ , $\sinh \gamma$ and $\cosh \gamma$ approach each other, so that by comparing (1.18) and (1.19), we see that the energy approaches $(aa/g/aa)$, as we previously stated.

It helps one's understanding of the nature of this special state if one sees how the quantities $F_{aa}(n)$ depend on n , for increasing values of the ratio $-(aa/g/aa)/4 \mathcal{E}_a$ of the repulsive interaction to the band width. In Fig. 1-2, we show these functions, for a series of increasing values of this ratio. The actual values of $F_{aa}(n)$ alternate in sign from one value of n to the next, and in the interest of clarity, this alternation is not shown, but only the

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

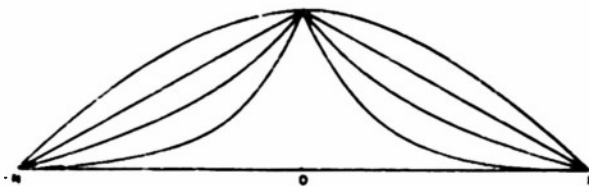


Fig. 1-2

$F_{aa}(n)$ as a function of n , for highest singlet level, different values of repulsive interaction.

magnitude of the F 's. For no repulsive interaction, the curve is the simple sine curve, reducing to zero for $n = \pm N$, and having a maximum for $n = 0$. As the repulsion increases in proportion to the band width, the curves become flatter, being made up of sine curves of longer and longer wavelength, until finally they become straight lines, the case of an infinitely long wavelength, which is the limiting case $\alpha = \pi$ or $\gamma = 0$. Then as γ builds up, they start to fall off exponentially as we go away from the origin, this falling off becoming steeper as the repulsion increases, or the band width decreases. For infinite repulsion, or zero band width, the falling off is infinitely rapid, only the case of $\tilde{R}_p = 0$ giving a non-vanishing contribution. The curves of Fig. 1-2 are of course not normalized, but are adjusted to give the same values for $\tilde{R}_p = 0$, in order to make a clear picture of what is going on.

Let us next consider the values of the quantities $F_{aa}(0)$ for the other singlet states; we have seen that as the detached ionic state builds up, these other singlets will approach zero at $R_p = 0$. We can investigate this at once from Eq. (1.14). We have already seen, from our discussion of Fig. 1-1, that as the repulsion increases, the values of α for the singlet states approach the values $m\pi/N$, where M is an integer. Since $F_{aa}(0) = \sin \alpha N$, this means that $F_{aa}(0)$ approaches $\sin m\pi = 0$. In other words, the correlation effect on all these states is at once obvious. It is not hard to set up approximate solutions for α holding for large repulsions, or small band widths, so as to see just how $F_{aa}(0)$ goes to zero with decreasing band width, but since our present case is not a quantitatively correct description of the actual situation, this is hardly worthwhile. When future three-dimensional calculations are made with the aim of real quantitative accuracy, it will be worthwhile investigating the use of the completeness relation to find the values of the $F_{aa}(0)$'s in detail. It should not be hard, even in this case, to approximate the solution for the separated state, and to use this in finding the $F_{aa}(0)$'s.

We have now investigated the case where both electrons are in the same non-degenerate band, and have concluded, as in Ref. 1, that it does not lead to ferromagnetism. Fortunately much of the analysis can be used again in considering the degenerate band, to which we now proceed. Let us assume that there are two bands, a and b , which must both be used in the expansion of the wave function. Thus we must consider F_{aa} , F_{ab} , F_{ba} , and F_{bb} ; but we can eliminate F_{ba} by use of Eq. (1.9). Let us set up the equation similar to Eq. (1.12) for this case, making the same assumption as before that the integrals involving the g 's are to be

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

disregarded unless all four Wannier functions are on the same atom. We find for the singlets

$$\sum_s 2 \mathcal{O}_a(\vec{R}_s) F_{aa}(\vec{R}_p - \vec{R}_s) + \delta(\vec{R}_p, 0) \left[(aa/g/aa) F_{aa}(\vec{R}_p) + 2(aa/g/ab) F_{ab}(\vec{R}_p) + (aa/g/bb) F_{bb}(\vec{R}_p) \right] = EF_{aa}(\vec{R}_p) \quad (1.20)$$

$$\sum_s \left[\mathcal{O}_a(\vec{R}_s) + \mathcal{O}_b(-\vec{R}_s) \right] F_{ab}(\vec{R}_p - \vec{R}_s) + \delta(\vec{R}_p, 0) \left[(ab/g/aa) F_{aa}(\vec{R}_p) + \left\{ (ab/g/ab) + (ab/g/ba) \right\} F_{ab}(\vec{R}_p) + (ab/g/bb) F_{bb}(\vec{R}_p) \right] = EF_{ab}(\vec{R}_p) \quad (1.21)$$

$$\sum_s 2 \mathcal{O}_b(\vec{R}_s) F_{bb}(\vec{R}_p - \vec{R}_s) + \delta(\vec{R}_p, 0) \left[(bb/g/aa) F_{aa}(\vec{R}_p) + 2(bb/g/ab) F_{ab}(\vec{R}_p) + (bb/g/bb) F_{bb}(\vec{R}_p) \right] = EF_{bb}(\vec{R}_p) \quad (1.22)$$

and for the triplets

$$\sum_s 2 \mathcal{O}_a(\vec{R}_s) F_{aa}(\vec{R}_p - \vec{R}_s) = EF_{aa}(\vec{R}_p) \quad (1.23)$$

$$\sum_s \left[\mathcal{O}_a(\vec{R}_s) + \mathcal{O}_b(-\vec{R}_s) \right] F_{ab}(\vec{R}_p - \vec{R}_s) + \delta(\vec{R}_p, 0) \left[(ab/g/ab) - (ab/g/ba) \right] F_{ab}(\vec{R}_p) = EF_{ab}(\vec{R}_p) \quad (1.24)$$

$$\sum_s 2 \mathcal{O}_b(\vec{R}_s) F_{bb}(\vec{R}_p - \vec{R}_s) = EF_{bb}(\vec{R}_p) \quad (1.25)$$

The equations for the triplets are separated from each other, but those for the singlets are not. Let us first inquire what can be done about this. To see how to proceed, we must look a little more carefully at the type of overlapping bands which we are likely to have. A case of accidental degeneracy is so unlikely as to be rather unimportant; it is discussed by H. Statz in his contribution to the present Report. The cases which are significant are those where, at the bottom of the band, there are two or more degenerate levels arising from crystal symmetry. A simple example in the two-dimensional Mathieu problem has been discussed earlier by the writer; ⁽⁴⁾ this is the case of degeneracy arising from an atomic p_x and p_y

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

function, and is typical of the sort of degeneracy which we shall really encounter in the ferromagnetic metals, though of course the problem there, arising from d-electron degeneracy in three dimensions, is more complicated. In Ref. 4, it was shown that in defining the Wannier function in such a case, we may if we choose consider one band to consist of the lower energy state for each point in the Brillouin zone, the other band to consist of the higher energy state at each point. In such a case the resulting Wannier functions, as well as the energies as functions of k , show the complete symmetry of the lattice. However, Koster⁽⁵⁾ has pointed out that it is not necessary to proceed in this way, and in fact it is not always desirable. We can instead set up energy surfaces which are discontinuous along certain 45° lines (in a two-dimensional Brillouin zone) or certain planes (in a three-dimensional case), combining the lower of the two energy surfaces on one side of this line with the higher one on the other, in such a way that the resulting energy surfaces transform into each other in the same way as the atomic p_x and p_y functions, under the various symmetry operations of the crystal. If we choose the energy bands in this way, the resulting Wannier functions also transform like p_x and p_y functions, and in fact reduce to those functions in the limit of infinite interatomic distance. For the present purpose, this second type of treatment is more appropriate, since it exhibits the degeneracy in an obvious way.

If we suppose, then, that the band a corresponds to that generated by atomic p_x -like functions, and b to that generated by p_y -like functions, we can at once draw certain conclusions about some of the matrix components on grounds of symmetry. Thus the components like $(ab/g/aa)$ contain just one factor, the function symbolized by b , which changes sign on reflection in the plane $y = 0$, so that the integrals must change sign when the sign of y is unchanged. On the other hand, this merely changes the name of one of the variables of integration, so that it cannot change the value of the integral, which consequently must equal zero. The same is true, as we see by inspection of Eqs. (1.20), (1.21), (1.22), of each component connecting an F_{ab} with either F_{aa} or F_{bb} . Consequently we see that (1.20) and (1.22) become equations for F_{aa} and F_{bb} only, while (1.21) is an equation for F_{ab} only. Furthermore, since the states a and b differ only by a rotation, there will be a degeneracy between Eqs. (1.20) and (1.22). We find easily that this degeneracy is to be removed by assuming that $F_{bb}(R_p) = \pm F_{aa}(R_p)$. When we insert these assumptions, Eq. (1.20) and (1.22) reduce to

$$\sum_s 2 \delta_s(R_s) F_{aa}(R_p - R_s) + \delta(R_p, 0) \left[(aa/g/aa) \pm (aa/g/bb) \right] F_{aa}(R_p) = E F_{aa}(R_p) \quad (1.26)$$

Furthermore, Eq. (1.21) reduces to

$$\sum_s \left[\delta_s(R_s) + \delta_b(-R_s) \right] F_{ab}(R_p - R_s) + \delta(R_p, 0) \left[(ab/g/ab) + (ab/g/ba) \right] F_{ab}(R_p) = E F_{ab}(R_p). \quad (1.27)$$

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

We now see that all the equations which we finally must solve are of the same form as that for the single band, which we discussed earlier. As in that case, we may use the one-dimensional case as a guide in understanding the solution; a problem with p_x and p_y -like functions in atoms arranged along the z axis would show the desired behavior. In such a case, the quantities $\mathcal{E}_a(R_s)$ and $\mathcal{E}_b(R_s)$ will be equal, so that Eqs. (1.26) and (1.27) will have the same non-diagonal matrix components. In discussing our solutions, let us first take the case where one electron is in each band, so that we are finding F_{ab} from Eq. (1.24) for the triplet, (1.27) for the singlet. We remember that for this case, no symmetry requirements are imposed on F_{ab} on account of the symmetry or antisymmetry of the wave function ψ . The nature of the Eqs. (1.24) and (1.27), which have inversion symmetry, demands that the solutions be either symmetric or antisymmetric on inversion, and we can have symmetric solutions for both the singlet and triplet, so that from our earlier discussion we know that the lowest symmetric solution will represent the lowest energy level of the problem. We now notice that the repulsive interaction in the singlet case is $(ab/g/ab) + (ab/g/ba)$ and in the triplet case $(ab/g/ab) - (ab/g/ba)$. Since the exchange integral $(ab/g/ba)$ is positive, this means a smaller repulsive interaction in the triplet. The main consequence of our study of the one-dimensional case was the result that the energy increased as the repulsive interaction increased (since this increased the value of α), so that we conclude unambiguously that of these two states, the triplet lies lower. We cannot conclude that it is the lowest energy level of the problem, however, until we have examined the other singlets, arising from the case where both electrons are in the same state a , to be sure that they do not lie even lower than this triplet.

These other two singlets are given by Eq. (1.26), and correspond again to symmetric solutions, with the repulsive interaction $(aa/g/aa) \pm (aa/g/bb)$. We can now see easily that these repulsive interactions are greater than with the solutions we have just considered, in which the repulsive interactions were $(ab/g/ab) \pm (ab/g/ba)$. In the first place, as we can see from the definitions, $(aa/g/bb) = (ab/g/ba)$, so that the separation of levels in either case is the same, and the order of levels will be determined by the two repulsive interactions $(aa/g/aa)$ and $(ab/g/ab)$. The first of these is the interaction of a charge distributed on orbital a , with itself; the second the interaction of a charge distributed on orbital a with another on orbital b . It seems plausible that the second would be smaller than the first, and calculation in special cases shows that this is indeed the case. Thus, if the two functions a and b are atomic p_x and p_y functions, we can find these various quantities in terms of the well-known F integrals. We find that $(aa/g/aa)$ equals $F^0 + 4/25 F^2$, $(ab/g/ab)$ equals $F^0 - 2/25 F^2$, so that in fact the second is smaller than the first in this case. Furthermore we find in this special case that $(aa/g/bb) = (ab/g/ba) = 3/25 F^2$, so that the repulsive interactions for the three singlets are $F^0 + 7/25 F^2$, $F^0 + 1/25 F^2$, and $F^0 + 1/25 F^2$; for the triplet, it is $F^0 - 5/25 F^2$. On the basis of the magnitudes of the repulsive interactions, we should certainly say in this case that the triplet state was the lowest, and that we should have

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

ferromagnetism.

Let us now use our study of the present problem to deepen our understanding of the nature of the ferromagnetic interaction in an actual ferromagnetic substance. According to the naive energy band theory, the question as to whether a given system is ferromagnetic or not is ordinarily answered as follows. We start with an energy band partly full of electrons, with equal numbers of electrons of each spin, so that it is unmagnetized. Then we reverse the spin of one electron, and ask whether the energy increases or decreases; if it increases, we conclude that it is not a ferromagnetic system, while if it decreases, we may reasonably expect that further reversals of spin will still further reduce the energy, resulting in a magnetized state as that of lowest energy, or a ferromagnetic system. According to the energy band theory, the energy changes for two reasons when one spin is reversed. First, there are additional exchange integrals between electrons of parallel spin, to be subtracted, so that the energy decreases. The leading term in these exchange integrals is an intra-atomic term like our quantity $(ab/g/ba)$, which retains its value to infinite internuclear separation. Secondly, the one-electron or Fermi energy will increase when the spin reverses, for the electron will be removed from a position below the Fermi level, and must be placed at an energy above the Fermi level when its spin is reversed, on account of the exclusion principle.

This increase of Fermi energy is greater, the broader the energy bands, so that we see easily that for very broad bands ferromagnetism is impossible, according to the energy band theory. At large distances, however, the increase of Fermi energy goes to zero, as the bands narrow, while the exchange term remains of the same size, arising from an intra-atomic effect. Thus the naive theory would predict that any substance should be ferromagnetic at large internuclear distances, an absurd prediction. The writer has pointed out⁽⁶⁾ that this absurdity is removed when we take account of configuration interaction, and in the present simple case we see just how to do this. As the internuclear distance increases, we have seen that the two electrons, rather than finding themselves on the same atom as often as would be predicted by the energy band theory without correlation, actually tend to avoid each other, and in the limit of infinite distance they are never found on the same atom, so that the intra-atomic exchange integral must be multiplied by a factor, $[F_{ab}(0)]^2$, measuring the probability of finding the ionic state, which decreases to zero with infinite interatomic distance. At the actual interatomic distance in a ferromagnetic crystal, however, it seems not unlikely that this factor has not decreased very much as compared to its value on the simple energy-band theory, so that while the tendency to ferromagnetism is decreased somewhat on account of this correlation effect, it still remains of the same order of magnitude as found in the energy band theory. A similar conclusion was reached in an earlier treatment using a less realistic model.⁽⁷⁾

If we make this modification, the energy band theory should be approximately valid. In particular, the increase in Fermi energy when we magnetize the system remains approximately as in that theory, so that the conclusion that ferromagnetism is impossible with broad

(A TWO-ELECTRON EXAMPLE OF FERROMAGNETISM)

bands remains unchanged. For a trivial reason, however, this increase in Fermi energy has not appeared in the present calculations. The reason is that we are dealing with only two electrons, which must be in the bottom of the Fermi band in the lowest energy level of the system, which alone we have considered; and we are dealing with at least a two-fold degenerate band. Thus, with our two bands a and b, the two electrons can have their spins parallel, and yet one can be in the lowest state of band a, the other in the lowest state of band b, so that in this special case it does not increase the Fermi energy to set their spins parallel. This is a special case arising from our two-electron problem, and does not in any way affect the validity of the general argument.

References

1. H. Statz, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., January 15, 1953, p. 23.
2. G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., January 15, 1953, p. 31.
3. J. C. Slater and W. Shockley, Phys. Rev. 50, 705 (1936).
4. J. C. Slater, Phys. Rev. 87, 807 (1952); see particularly pp. 827-831.
5. G. F. Koster, Phys. Rev. 89, 67 (1953).
6. J. C. Slater, Revs. Modern Phys., January 15, 1953. See also Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., July 15, 1952, p. 17.
7. J. C. Slater, Phys. Rev. 52, 198 (1937).

J. C. Slater

2. A SIMPLE MODEL OF FERROMAGNETISM

In the last Progress Report, ⁽¹⁾ we have asked the question, if two electrons in accidentally degenerate bands of different width will or will not align their spins? In all practical cases the bottoms of the two bands will not coincide and will have a finite energy difference. One can predict without any calculation that both electrons will move in the lower lying band and will set their spins antiparallel. If we consider the artificial case in which the two bottoms of the bands coincide then the question whether the triplet or the singlet has lower energy depends essentially on the difference in width of the two bands. The mathematical problem is identical to that solving an atomic multiplet problem. Using this analogy we have two orbitals with different one-electron energies. The question is now: do the electrons rather prefer to stay in the same orbitals with opposite spins or is the gain in "exchange" energy large enough to overcome the energy loss to bring one electron with reversed spin in the higher orbital? When the orbitals have the same one-electron energies we know from Hund's rule that the electrons will set their spins parallel even if all configurations are taken into account. We therefore expect to find the triplet state lying lowest only for those orbitals which have small differences in energy. In the mathematical description the difference in energy of the two orbitals comes from the different structure of the two bands. One can see this without any calculation by considering the expansion of the wave function (describing the movement of the two electrons in the crystal) in products of Bloch functions. In our picture the orbital energies are essentially represented by the weighted sums over Bloch-function energies. If one band is now considerably broader then all Bloch functions have higher energies and the corresponding orbital has a higher energy too. We may therefore expect to have orbitals of approximately the same energy only when the two bands have the same width. Such cases of accidental degeneracy are never found in real crystals. The 4s band in the iron group elements, for example, is always much broader than the 3d bands. So we expect, at least in the two-electron model, to have only ferromagnetic alignment of spins in bands which are degenerate because of the crystalline symmetry. The detailed description of this case the reader may find in the publication already mentioned.

Reference

1. H. Statz, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 23.

H. Statz

3. THEORY OF FERROMAGNETISM

The work reported in the previous Progress Report has been mostly finished. The free energy was minimized with respect to parameters and the Curie temperature T_C was shown to be determined by the following equation

$$\exp(2J'/kT_C) = \omega/(\omega - 2) \quad (3.1)$$

where J' plays the role of the exchange integral of Heisenberg's model and is defined by

$$J' = J \left[1 - \frac{2\omega K - K_{55}}{8\omega J} - \left\{ \left(\frac{2\omega K - K_{55}}{8\omega J} \right)^2 + \left(\frac{K_{54} + Q}{J} \right)^2 \right\}^{1/2} \right] \quad (3.2)$$

K , K_{55} , K_{54} , Q , and J are defined in the previous Progress Report, ⁽¹⁾ and 2ω is the coordination number of the lattice.

K_{55} is an atomic quantity and does not depend on the internuclear distance, but the Coulomb integral K and the exchange integral J become small as the internuclear distance becomes large. For large internuclear distances, Eq. (3.2) can be reduced to

$$J' = J - 4\omega(K_{54} + Q)^2/K_{55} \quad (3.3)$$

which has close similarity to the equation derived by Slater ⁽²⁾

$$J' = J - 2W_R^2/K_{55} \quad (3.4)$$

W_R^2 in Eq. (3.4) and $(K_{54} + Q)^2$ in Eq. (3.3) are both related to the width of the band, increasing as the internuclear distance becomes smaller. This similarity gives indirect support of the present treatment.

As is seen from Eq. (3.1), it is necessary and sufficient that J' is positive in order for the ferromagnetic state to appear. As an example, the case of a simple cubic lattice was calculated with a Gaussian orbital function at a lattice point. This atomic orbital was orthogonalized and the integrals Q , K , J , etc. were calculated using these OAO's. Putting these numbers in Eq. (3.2), it was shown that the ferromagnetic state does not appear for any internuclear distance. This result confirms the conclusion derived by Slater, Statz and Koster. ⁽³⁾

Though this treatment does not give results which qualitatively contradict those of other authors, this treatment has unclarified assumptions in its foundation. These shortcomings are to be investigated at some future time.

(THEORY OF FERROMAGNETISM)

References

1. R. Kikuchi, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 41.
2. J. C. Slater, Phys. Rev. 52, 198 (1937), Eq. (31).
3. J. C. Slater, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 1; *ibid.*, p. 23; G. F. Koster, *ibid.*, p. 31.

R. Kikuchi

4. A SPIN OPERATOR METHOD

Let us assume that we are dealing with a $2N$ electron problem and are interested in applying the methods of configuration interaction to the system in order to find the ground state. One of the first problems in such an investigation is that of spin degeneracy. For a set of $2N$ orbitals and $2N$ electrons it is possible to form many states of a given multiplicity by associating either α or β spin with the collection of orbitals in a variety of ways. The present discussion will be restricted to the consideration of the singlet states. Under the conditions cited above one can construct

$$\frac{(2N)!}{N!(N+1)!}$$

orthogonal singlet states.

One means of setting up all of the singlets is the valence-bond method which leads to the correct number of linearly independent singlets, but the states so obtained are not orthogonal. Another method of constructing all of the singlets is by using the branching diagram, a pictorial description of adding the spin angular momentum of electrons one by one which shows for any number of electrons how many states of various multiplicities there are and what the parentage of the state is. The method of the branching diagram will be used in the following discussion.

A spin operator method is given here for setting up all of the orthogonal singlets for a $2N$ electron problem. The five orthogonal singlets corresponding to a six electron system are analyzed in some detail and from this analysis a spin operator O is derived which when operating on a single determinant creates an eigenfunction of S^2 . All of the singlets for the six electron problem are written down in terms of this operator as well as the fourteen orthogonal singlets for the eight electron problem. The operator O is quite general and has very useful properties. In the latter part of this report some of the applications of this operator to the problem of configuration interaction are discussed.

In Fig. 4-1 the branching diagram for a six-electron system is given. This diagram not only shows how many states of a given multiplicity there are for n electrons, but by applying the methods of vector addition of angular momentum, the branching diagram also shows how the states are actually constructed. In Figs. 4-1a through 4-1e the five possible ways of obtaining a singlet state for the six-electron problem are illustrated. Let us consider in some detail the state described in Fig. 4-1a. The branching diagram tells us that this state results from the combination of two three-electron systems, say A and B , each of which are in a state of $S = 3/2$. Let us order the six orbitals for this problem $\phi_1, \phi_2, \phi_3, \phi_4, \phi_5$ and ϕ_6 . These orbitals are assumed to be orthonormal and distinct. Let ϕ_1, ϕ_2 , and ϕ_3 and three electrons make up set A and ϕ_4, ϕ_5 , and ϕ_6 and three electrons comprise set B . The singlet in Fig. 4-1a can be expressed as

(A SPIN OPERATOR METHOD)

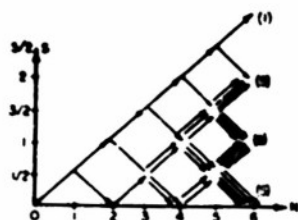


Fig. 4-1

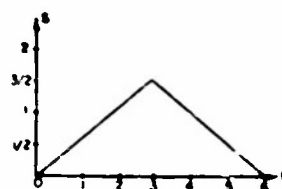


Fig. 4-1a

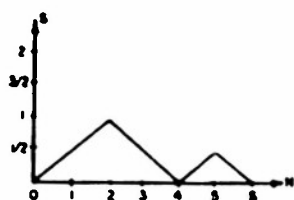


Fig. 4-1b

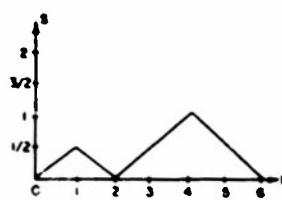


Fig. 4-1c

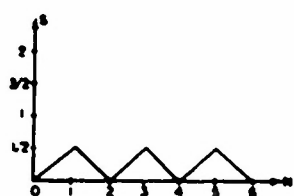


Fig. 4-1d

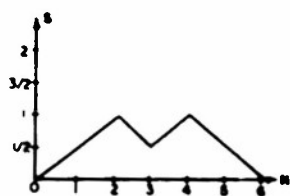


Fig. 4-1e

$$\begin{aligned}
 \psi_1(S=0) = & C_0 \phi_A(S=3/2, M_S=3/2) \cdot \phi_B(S=3/2, M_S=-3/2) \\
 & + C_1 \phi_A(S=3/2, M_S=1/2) \cdot \phi_B(S=3/2, M_S=-1/2) \\
 & + C_2 \phi_A(S=3/2, M_S=-1/2) \cdot \phi_B(S=3/2, M_S=+1/2) \\
 & + C_3 \phi_A(S=3/2, M_S=-3/2) \cdot \phi_B(S=3/2, M_S=+3/2)
 \end{aligned} \tag{4.1}$$

The states represented by $\phi_A(S, M_S)$ and $\phi_B(S, M_S)$ are

$$\phi_A(S=3/2, M_S=3/2) = \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) & \phi_1(3)\alpha(3) \\ \phi_2(1)\alpha(1) & \phi_2(2)\alpha(2) & \phi_2(3)\alpha(3) \\ \phi_3(1)\alpha(1) & \phi_3(2)\alpha(2) & \phi_3(3)\alpha(3) \end{vmatrix} = |\alpha\alpha\alpha|. \tag{4.2}$$

$$\phi_B(S=3/2, M_S=-3/2) = \begin{vmatrix} \phi_4(4)\beta(4) & \phi_4(5)\beta(5) & \phi_4(6)\beta(6) \\ \phi_5(4)\beta(4) & \phi_5(5)\beta(5) & \phi_5(6)\beta(6) \\ \phi_6(4)\beta(4) & \phi_6(5)\beta(5) & \phi_6(6)\beta(6) \end{vmatrix} = |\beta\beta\beta|. \tag{4.3}$$

(A SPIN OPERATOR METHOD)

$$\phi_A(S = 3/2, M_S = 1/2) = \frac{1}{\sqrt{3}} [\beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta] \quad (4.4)$$

$$\phi_B(S = 3/2, M_S = -1/2) = \frac{1}{\sqrt{3}} [\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta] \quad (4.5)$$

$$\phi_A(S = 3/2, M_S = -1/2) = \frac{1}{\sqrt{3}} [\alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha] \quad (4.6)$$

$$\phi_B(S = 3/2, M_S = +1/2) = \frac{1}{\sqrt{3}} [\alpha\alpha\beta + \beta\alpha\alpha + \alpha\beta\alpha] \quad (4.7)$$

$$\phi_A(S = 3/2, M_S = -3/2) = \beta\beta\beta \quad (4.8)$$

$$\phi_B(S = 3/2, M_S = +3/2) = \alpha\alpha\alpha \quad (4.9)$$

All determinants are assumed to be normalized.

The expression $\phi_A(S = 3/2, M_S) \cdot \phi_B(S = 3/2, -M_S)$ involves the combination of the determinants which make up the states. The "product" of two determinants is taken to mean

$$|\alpha\beta\alpha| \cdot |\beta\beta\alpha| = \begin{vmatrix} \phi_1(1)\alpha(1) & \dots & \phi_1(6)\alpha(6) \\ \phi_2(1)\beta(1) & \dots & \phi_2(6)\beta(6) \\ \phi_3(1)\alpha(1) & \dots & \phi_3(6)\alpha(6) \\ \phi_4(1)\beta(1) & \dots & \phi_4(6)\beta(6) \\ \phi_5(1)\beta(1) & \dots & \phi_5(6)\beta(6) \\ \phi_6(1)\alpha(1) & \dots & \phi_6(6)\alpha(6) \end{vmatrix} \quad (4.10)$$

In general the "product" of an $n \times n$ determinant and an $m \times m$ determinant is an $(m + n)$ $(m + n)$ determinant. We also note that the order must be preserved, i. e. $|\alpha\beta\alpha| \cdot |\beta\beta\alpha|$ is not equal to $|\beta\beta\alpha| \cdot |\alpha\beta\alpha|$. It is to be borne in mind that the $\phi(S, M_S)$ are normalized states of definite multiplicity. The coefficients C_i in (4.1) are the transformation amplitudes for the vector addition of angular momentum, and sometimes called the Clebsch-Gordon coefficients. They may be obtained in this case from the general expression for combining two systems of spin S to form a resultant singlet. This is

$$\psi_{S=0} = \sum_{M_S=-S}^{+S} (-1)^{S-M_S} \phi_A(S, M_S) \cdot \phi_A(S, -M_S) \quad (4.11)$$

Let us now look into the question of forming the various $\phi_{A,B}(S, M_S)$ states. $\phi_A(S = 3/2, M_S = 1/2)$ is obtained by the step-down operator acting on $\phi_A(S = 3/2, M_S = 3/2)$ and

(A SPIN OPERATOR METHOD)

$\phi_B(S = 3/2, M_S = -1/2)$ is gotten by the step-up operator acting on $\phi_B(S = 3/2, M_S = -3/2)$. Thus except for a constant we have

$$\phi_A(S = 3/2, M_S = 1/2) = S_A^- \phi_A(S = 3/2, M_S = 3/2)$$

$$\phi_B(S = 3/2, M_S = -1/2) = S_B^+ \phi_B(S = 3/2, M_S = -3/2)$$

where $S_A^- = S_1^- + S_2^- + S_3^-$ and $S_B^+ = S_4^+ + S_5^+ + S_6^+$. Writing this out we get

$$S_A^- |a\alpha a| = [|\beta a \alpha| + |a \beta a| + |a a \beta|] \quad (4.12)$$

$$S_B^+ |\beta \beta \beta| = [|\alpha \beta \beta| + |\beta \alpha \beta| + |\beta \beta \alpha|] \quad (4.13)$$

In order to have normalized states, we must multiply the right-hand side of both (4.12) and (4.13) by $(3)^{-1/2}$ which is the number of ways of reversing one spin in set A or B taken to the $-1/2$ power. We can write the second term in (4.1) except for the factor of -1 as

$$\frac{(S_A^- S_B^+)}{3} \phi_A(S = 3/2, M_S = 3/2) \cdot \phi_B(S = 3/2, M_S = -3/2) \quad (4.14)$$

The third term in (4.1) may be written as

$$\frac{(S_A^- S_B^+)^2}{3 \times 4} \phi_A(S = 3/2, M_S = 3/2) \cdot \phi_B(S = 3/2, M_S = -3/2) \quad (4.15)$$

The factor of 3 in the denominator is the product of the number of ways of reversing two spins in set A taken to the $1/2$ power and the number of ways of reversing two spins in B taken to the $1/2$ power. The factor of 4 in the denominator arises because in the expansion of $(S_A^- S_B^+)^2$ we encounter equivalent terms of the type $S_1^- S_2^- S_4^+ S_5^+ + S_1^- S_2^- S_5^+ S_4^+ + S_2^- S_1^- S_4^+ S_5^+ + S_2^- S_1^- S_5^+ S_4^+$. Thus if there are M spin reversals in set A and in set B, we must divide out the permutations among set A and set B as in the case above.

The fourth term in (4.1) may be written

$$\frac{(S_A^- S_B^+)^3}{36} \phi_A(S = 3/2, M_S = 3/2) \cdot \phi_B(S = 3/2, M_S = -3/2) \quad (4.16)$$

Here there is just one way of reversing all the spins in A and in B. The factor of 36 in the denominator is necessary because there are $3!$ ways of expressing the reversals in A, i.e., $S_1^- S_2^- S_3^-$, $S_2^- S_1^- S_3^-$, etc. and $3!$ ways in B.

(A SPIN OPERATOR METHOD)

We can now combine (4.14), (4.15), and (4.16) and write the singlet (4.1) as

$$\begin{aligned} \psi_1(S=0) = & \left\{ (S_A^- S_B^+)^0 - \frac{1}{3} (S_A^- S_B^+)^1 + \frac{1}{12} (S_A^- S_B^+)^2 - \frac{1}{36} (S_A^- S_B^+)^3 \right\} \\ & \cdot \phi_A(S=3/2, M_S=3/2) \cdot \phi_B(S=3/2, M_S=-3/2). \end{aligned} \quad (4.17)$$

We must multiply the right-hand side of (4.17) by $1/2$ in order that the final state will be normalized.

We have now expressed the singlet shown in Fig. 4-1a as the result of an operator acting on the "product" of $\phi_A(S=3/2, M_S=3/2)$ and $\phi_B(S=3/2, M_S=-3/2)$. We seek now to generalize this operator to the $2N$ electron case. That is given a $2N$ electron system, a collection of N electrons and N orbitals will be termed as set A, and the remaining N electrons and N orbitals denoted by set B. We wish to form the $2N$ electron-orbital singlet state by combining sets A and B each of which is to be in a state of maximum multiplicity, i.e., $S_{A,B} = N/2$. Our composite state will be

$$\psi(S=0) = O_1 \left[\phi_A(S=\frac{N}{2}, M_S=\frac{N}{2}) \phi_B(S=\frac{N}{2}, M_S=-\frac{N}{2}) \right] \quad (4.18)$$

Denoting the number of spin reversals in A or B by M , the general form of the operator, which will be represented by O_1 , is

$$O_1 = \sum_{M=0}^N (-1)^M \frac{(N-M)!}{N! M! \sqrt{N+1}} (S_A^- S_B^+)^M \quad (4.19)$$

where

$$\begin{aligned} S_A^- &= S_{1A}^- + S_{2A}^- + \dots + S_{NA}^- \\ S_B^+ &= S_{1B}^+ + S_{2B}^+ + \dots + S_{NB}^+ \end{aligned} \quad (4.20)$$

The $(-1)^M$ is the Clebsch-Gordon coefficient. The factor $(N-M)!/N!M!$ is

$$\left[\frac{(N-M)! M!}{N!} \right]^{+1/2} \cdot \left[\frac{(N-M)! M!}{N!} \right]^{+1/2} \cdot \frac{1}{M!} \cdot \frac{1}{M!} \quad (4.21)$$

The first factor in (4.21) is the number of ways of making M reversals in set A, which contains N elements, taken to the $-1/2$ power. The second factor is the number of ways of making M reversals of spin in set B taken to the $-1/2$ power. The third factor divides out

(A SPIN OPERATOR METHOD)

equivalent permutations in set A, as explained above. The fourth factor does the same in set B.

Therefore, we have found an operator O_1 which, when acting on the "product" of two N electron systems each in a state of maximum S and one with $M_S = S$ and the other with $M_S = -S$, produces a composite state of 2N electrons which is a singlet. It turns out that the present operator O_1 is not general enough to be a really powerful tool. In the course of events a number of modifications will suggest themselves.

Let us now investigate the creation of the remaining singlets for the six-electron problem. The reader is referred to Figs. 4-1b, 4-1c, 4-1d, and 4-1e for a pictorial description of the structure of these states. In Fig. 4-1b our resultant singlet is the "product" of a singlet state made up of the first four orbitals and four electrons, and the singlet made from the last two orbitals and electrons. Eq. (4.11) shows that if we combine two systems each of which is in a singlet state to form a resultant singlet, that the composite state is merely the "product" of $\phi_1(S=0)$ and $\phi_2(S=0)$. Our plan is, therefore, to generate the two singlets inferred from Fig. 4-1b and to take their "product" to get the final state. The singlet formed from the first four orbitals and four electrons is the result of combining two states $\phi_A(S=1, M_S=1)$ and $\phi_B(S=1, M_S=-1)$. The singlet formed from the last two orbitals and two electrons is the result of combining two states $\phi_A(S=1/2, M_S=1/2)$ and $\phi_B(S=1/2, M_S=-1/2)$. Thus the six-electron singlet for Fig. 4-1b is simply

$$\psi_2(S=0) = O_1 |\alpha\beta\beta\alpha\rangle \cdot O'_1 |\alpha\beta\rangle \quad (4.22)$$

which when expanded is

$$\begin{aligned} \psi_2(S=0) = \frac{1}{\sqrt{6}} \left[|\alpha\beta\beta\alpha\rangle - \frac{1}{2} \left\{ |\alpha\beta\alpha\beta\rangle + |\alpha\beta\beta\alpha\rangle + |\beta\alpha\alpha\beta\rangle + |\beta\alpha\beta\alpha\rangle \right. \right. \\ \left. \left. + |\beta\beta\alpha\alpha\rangle \right\} \cdot \left[|\alpha\beta\rangle - |\beta\alpha\rangle \right] \right] \end{aligned} \quad (4.23)$$

For the purpose of illustration let us write out O_1 and O'_1 . For O_1 N = 2, and for O'_1 N = 1. Thus from (4.19) we get

$$\begin{aligned} O_1 = \frac{1}{\sqrt{3}} \left[1 - \frac{1}{2} \left\{ S_1^- S_3^+ + S_1^- S_4^+ + S_2^- S_3^+ + S_2^- S_4^+ \right\} + \frac{1}{4} \left\{ S_1^- S_2^- S_3^+ S_4^+ \right. \right. \\ \left. \left. + S_2^- S_1^- S_3^+ S_4^+ + S_1^- S_2^- S_4^+ S_3^+ + S_2^- S_1^- S_4^+ S_3^+ \right\} \right] \end{aligned}$$

Since $S_i^- S_j^+$ commute for $i \neq j$

$$O_1 = \frac{1}{\sqrt{3}} \left[1 - \frac{1}{2} \left\{ S_1^- S_3^+ + S_1^- S_4^+ + S_2^- S_3^+ + S_2^- S_4^+ \right\} + S_1^- S_2^- S_3^+ S_4^+ \right] \quad (4.24)$$

and O_1' is

$$O_1' = \frac{1}{\sqrt{2}} [1 - S_5^- S_6^+] \quad (4.25)$$

The singlet in Fig. 4-1c is constructed in the same manner as $\psi_2(S = 0)$ only now the first two orbitals and two electrons are combined to form a singlet, and the last four orbitals and four electrons are combined to form a singlet. The composite singlet is just the "product" of these singlets. Hence

$$\psi_3(S = 0) = O_1' |a\beta| \cdot O_1 |aa\beta\beta| \quad (4.26)$$

$$\begin{aligned} \psi_3(S = 0) = \frac{1}{\sqrt{6}} [|a\beta| - |\beta a|] \cdot [|aa\beta\beta| - \frac{1}{2} \{ |a\beta a\beta| + |a\beta\beta a| \\ + |\beta a\beta a| + |\beta a a\beta| \} + |\beta\beta a a|] \end{aligned} \quad (4.27)$$

Theorem I, which is proved in Appendix I, and which states that different paths on the branching diagram terminating at the same destination lead to orthogonal states, shows us that ψ_2 and ψ_3 are indeed orthogonal.

The singlet formed in Fig. 4-1d is gotten by taking the "product" of three singlets each made up of two orbitals and two electrons. Thus

$$\psi_4(S = 0) = O_1^{(1)} |a\beta| \cdot O_1^{(3)} |a\beta| \cdot O_1^{(5)} |a\beta| \quad (4.28)$$

where $O_1^{(i)}$ is

$$O_1^{(i)} = \frac{1}{\sqrt{2}} [1 - S_i^- S_{i+1}^+] \quad (4.29)$$

It is of interest to note that this state is one of the familiar valence-bond singlets. In valence-bond language one would describe the state as having a bond between ϕ_1 and ϕ_2 , a bond between ϕ_3 and ϕ_4 , and a bond between ϕ_5 and ϕ_6 . The expanded form of this state is

$$\psi_4(S = 0) = \frac{1}{\sqrt{8}} [(|a\beta| - |\beta a|) \cdot (|a\beta| - |\beta a|) \cdot (|a\beta| - |\beta a|)] \quad (4.30)$$

Let us now consider the last singlet, that shown in Fig. 4-1e. The singlets formed so far have been either the "product" of subsidiary singlets formed by the application of O_1 , or in the case of Fig. 4-1a, a total singlet formed directly by the use of O_1 . The state shown in 4-1e is the result of combining two states each made up of three orbitals and three electrons and both in a state of $S = 1/2$. Our plan is now to find out how to use O_1 so that it can

(A SPIN OPERATOR METHOD)

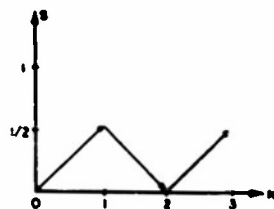


Fig. 4-2a

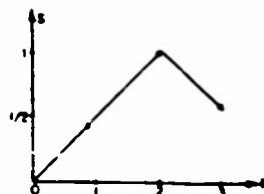


Fig. 4-2b

operate on a determinant made up of an odd number of electrons; therefore, not in a state of $M_S = 0$. We want the result of operating with O_1 on, for example, $|a\alpha\beta|$ to be a state of $\psi(S = 1/2)$. The formation of a state of $\psi(S = 1/2)$ from three electrons may be accomplished in two different ways as indicated by the branching diagram, Fig. 4-1. The two possible states are shown in Figs. 4-2a and 4-2b. The state illustrated in 4-2a is the result of the combination of a singlet formed by the first two orbitals and two electrons and a state $\phi(S = 1/2)$ formed from the third orbital and an electron. That is

$$\begin{aligned}\psi_{2a} &= \frac{1}{\sqrt{2}} [|a\beta| - |\beta a|] \cdot |a| \\ \psi_{2a} &= O_1 |a\beta| \cdot O_1 |a| = \{O_1 |a\beta|\} \cdot |a|\end{aligned}\quad (4.31)$$

The state shown in 4-2b is the result of the combination of a state $\phi(S = 1)$ formed from the first two electrons, and a state $\phi(S = 1/2)$ formed from the third orbital and an electron. The method of creating such a state by the vector addition of angular momentum is well known and the result is

$$\psi(S = 1/2, M_S = 1/2) = \frac{2}{\sqrt{6}} |a\alpha| \cdot |\beta| - \frac{1}{\sqrt{6}} [|a\beta| + |\beta a|] \cdot |a| \quad (4.32)$$

We can factor this state as follows

$$\psi(S = 1/2, M_S = 1/2) = \frac{1}{\sqrt{6}} \{ |a| \cdot (|a\beta| - |\beta a|) + (|a \cdot |a| \cdot |\beta| - |\beta \cdot |a| \cdot |a|) \} \quad (4.33)$$

This defines a new way of writing a "product", for example

$$|a\beta| \cdot \{ |a\beta| - |\beta a| \} \cdot |\beta\beta| = |a\beta a\beta\beta\beta| - |a\beta\beta a\beta\beta| \quad (4.34)$$

We can generate the state $\psi(S = 1/2, M_S = 1/2)$ by the application of an operator which is

$$(1 - S_2^- S_3^+) + (1 - S_1^- S_3^+) \quad (4.35)$$

(A SPIN OPERATOR METHOD)

which operates on $|aa\beta|$. We have

$$(1 - S_2^- S_3^+) |aa\beta| = |aa\beta| - |a\beta a|$$

$$(1 - S_1^- S_3^+) |aa\beta| = |aa\beta| - |\beta aa|$$

Therefore, except for the proper normalization constant

$$\left[(1 - S_2^- S_3^+) + (1 - S_1^- S_3^+) \right] |aa\beta| = 2|aa\beta| - |a\beta a| - |\beta aa| \quad (4.36)$$

Thus the state $\psi(S = 1/2, M_S = 1/2)$ can be created by use of O_1 since (4.36) can be written

$$\begin{aligned} \psi(S = 1/2, M_S = +1/2) &= \frac{1}{\sqrt{3}} \left[O_1^{(2,3)} + O_1^{(1,3)} \right] |aa\beta| \\ &= \frac{1}{\sqrt{6}} \left[2|aa\beta| - |a\beta a| - |\beta aa| \right] \end{aligned} \quad (4.37)$$

$$\begin{aligned} \psi(S = 1/2, M_S = -1/2) &= \frac{1}{\sqrt{3}} \left[O_1^{(4,5)} + O_1^{(4,6)} \right] |a\beta\beta| \\ &= \frac{1}{\sqrt{6}} \left[2|a\beta\beta| - |\beta a\beta| - |\beta\beta a| \right] \end{aligned} \quad (4.38)$$

Having found the two states $\psi(S = 1/2, M_S = \pm 1/2)$ corresponding to those involved in the formation of the singlet in $\psi_5(S = 0)$ Fig. 4-1e, we can create the composite six-electron singlet as

$$\psi_5(S = 0) = O_1 \left[\psi(S = 1/2, M_S = 1/2) \cdot \psi(S = 1/2, M_S = -1/2) \right] \quad (4.39)$$

When written out, this is

$$\begin{aligned} \psi_5(S = 0) &= \frac{O_1}{6} \left[4|aa\beta a\beta\beta| - 2|aa\beta\beta a\beta| - 2|aa\beta\beta\beta a| - 2|a\beta aa\beta\beta| \right. \\ &\quad \left. + |a\beta a\beta a\beta| + |a\beta a\beta\beta a| - 2|\beta aaaa\beta\beta| + |\beta aa\beta a\beta| + |\beta aa\beta\beta a| \right] \end{aligned} \quad (4.40)$$

where the orbitals associated with α spin comprise set A and the orbitals associated with spin β comprise set B. For example the first determinant in (4.40) has $\phi_1, \phi_2,$ and ϕ_4 in A and $\phi_3, \phi_5,$ and ϕ_6 in B.

(A SPIN OPERATOR METHOD)

With expression (4.40) we have completed the task of writing down all of the orthogonal singlets for the six-electron case with the help of the operator O_1 . Now we wish to generalize this operator so that it can be used for a wider variety of situations. Eqs. (4.37), (4.38) and (4.40) show that it is sometimes necessary to use more than one definition of sets A and B. It would be much more convenient to have a form of O_1 which would automatically operate on all possible choices for sets A and B. We can easily modify O_1 to do this and the generalized form of O_1 will be written as O. It is

$$O = \frac{1}{(N+1)^{1/2}} \sum_i \left[1 + \sum_{M=1}^N \frac{(-1)^M (N-M)!}{N! M!} \left\{ (S_{A_i}^- S_{B_i}^+)^M + (S_{A_i}^+ S_{B_i}^-)^M \right\} \right. \\ \left. \prod_{j_{A_i}, k_{B_i}} (S_{j_{A_i}}^+ S_{j_{A_i}}^- S_{k_{B_i}}^- S_{k_{B_i}}^+ + S_{j_{A_i}}^- S_{j_{A_i}}^+ S_{k_{B_i}}^+ S_{k_{B_i}}^-) \right] \quad (4.41)$$

where the sum over i is the sum over all different divisions of the orbitals ϕ_1 to ϕ_{2N} into two groups of N orbitals. O is to operate on a determinant with total M_S equal to zero. The rules for applying O to determinants with total M_S not zero will be given in a later section. The properties of O will now be written down and the proofs of these statements is given in the various appendices.

- I. O is hermetian.
- II. O commutes with S^2 .
- III. O commutes with the Hamiltonian H .
- IV. O^2 equals $(N+1)^{1/2} \left\{ n(1 + \frac{n-1}{N+1}) \right\}^{1/2} O$. (1)
- V. O commutes with the antisymmetrizing operator A .

We are now in a position to illustrate how O operates on a determinant. Consider for example O operating on $\alpha\beta\alpha\beta$. First, since O commutes with the antisymmetrizing operator, we can write $O\alpha\beta\alpha\beta$ as $AO\phi_1(1)\alpha(1)\phi_2(2)\beta(2)\phi_3(3)\alpha(3)\phi_4(4)\beta(4)$ where O now operates on a spin-product function. We can divide our four orbitals ϕ_1, ϕ_2, ϕ_3 , and ϕ_4 into two groups in three different ways $\phi_1, \phi_2 - \phi_3, \phi_4; \phi_1, \phi_3 - \phi_2, \phi_4; \phi_1\phi_4 - \phi_2, \phi_3$. Let us first consider the

$$\prod_{j_{A_i}, k_{B_i}}^N (S_{j_{A_i}}^+ S_{j_{A_i}}^- S_{k_{B_i}}^- S_{k_{B_i}}^+ + S_{j_{A_i}}^- S_{j_{A_i}}^+ S_{k_{B_i}}^+ S_{k_{B_i}}^-)$$

part of O operating on $\phi_1(1)\alpha(1)\phi_2(2)\beta(2)\phi_3(3)\alpha(3)\phi_4(4)\beta(4)$. Suppose we take the division $\phi_1\phi_2 - \phi_3, \phi_4$ and let ϕ_1 and ϕ_2 comprise set A, and ϕ_3 and ϕ_4 make up set B. Then we have

(A SPIN OPERATOR METHOD)

$$\left[S_1^+ S_1^- S_2^+ S_2^- S_3^+ S_3^- S_4^+ S_4^- + S_1^- S_1^+ S_2^- S_2^+ S_3^- S_3^+ S_4^- S_4^+ \right] \phi_1(1) \alpha(1) \phi_2(2) \beta(2) \phi_3(3) \alpha(3) \phi_4(4) \beta(4) \quad (4.42)$$

This is clearly zero. Hence this choice of dividing our four orbitals into two groups yields nothing. Similarly the choice $\phi_1, \phi_4 - \phi_2, \phi_3$ gives nothing. For the selection $\phi_1, \phi_3 - \phi_2, \phi_4$ we have

$$\begin{aligned} & \left[S_1^+ S_1^- S_3^+ S_3^- S_2^- S_2^+ S_4^- S_4^+ + S_1^- S_1^+ S_3^- S_3^+ S_2^+ S_2^- S_4^+ S_4^- \right] \phi_1(1) \alpha(1) \phi_2(2) \beta(2) \phi_3(3) \alpha(3) \phi_4(4) \beta(4) \\ & = \phi_1(1) \alpha(1) \phi_2(2) \beta(2) \phi_3(3) \alpha(3) \phi_4(4) \beta(4) . \end{aligned} \quad (4.43)$$

Thus when operating on a spin product function with the \prod_i operator, we get zero for all choices of i except one, which leaves the spin product function invariant. Let us now examine the factor $\left[(S_{A_i}^- S_{B_i}^+)^M + (S_{A_i}^+ S_{B_i}^-)^M \right]$. The term $(S_{A_i}^+ S_{B_i}^-)^M$ gives zero for all M since in this example we have associated a spin with all orbitals in set A . Thus we see that O effectively reduces to

$$O = \frac{1}{\sqrt{3}} \left[1 - \frac{1}{2} (S_1^- S_2^+ + S_1^- S_4^+ + S_3^- S_2^+ + S_3^- S_4^+) + S_1^- S_3^- S_2^+ S_4^+ \right]$$

which is the same as (4.24) if we interchange the 2's and 3's in that expression. One should note that we would have gotten the same result had we associated β spin with all orbitals in A . This is as it should be for the assignment of spin to set A or B is entirely arbitrary.

Using our new operator O let us look back at the five singlets we have set up for the six-electron problem. That originally given in (4.17) is just

$$\psi_1(S=0) = O | \alpha \alpha \alpha \beta \beta \beta | \quad (4.44)$$

Here O reduces to just the original operator. $\psi_2(S=0)$ given in (4.22) is

$$\psi_2(S=0) = O | \alpha \alpha \beta \beta | \cdot O | \alpha \beta | \quad (4.45)$$

$\psi_3(S=0)$ given in (4.26) is

$$\psi_3(S=0) = O | \alpha \beta | \cdot O | \alpha \alpha \beta \beta | \quad (4.46)$$

$\psi_4(S=0)$ given in (4.28) is

$$\psi_4(S=0) = O | \alpha \beta | \cdot O | \alpha \beta | \cdot O | \alpha \beta | \quad (4.47)$$

(A SPIN OPERATOR METHOD)

In the case of $\psi_5(S = 0)$ we encounter operands, i. e., $|aa\beta|$ or $|\alpha\beta\beta|$, with $M_S \neq 0$ as in (4.37) and (4.38). If we operate on $|aa\beta|$ with O , taking N to be 1 and letting the sum over i range over all possibilities of dividing the three orbitals into two groups with one orbital per group and excluding the remaining orbital, then the expanded form of O is

$$\begin{aligned} O = & \frac{1}{\sqrt{2}} (1 - \{S_1^- S_2^+ + S_1^+ S_2^-\}) (S_1^+ S_1^- S_2^- S_2^+ + S_1^- S_1^+ S_2^+ S_2^-) \\ & + \frac{1}{2} (1 - \{S_1^- S_3^+ + S_1^+ S_3^-\}) (S_1^+ S_1^- S_3^- S_3^+ + S_1^- S_1^+ S_3^+ S_3^-) \\ & + \frac{1}{2} (1 - \{S_2^- S_3^+ + S_2^+ S_3^-\}) (S_2^+ S_2^- S_3^- S_3^+ + S_2^- S_2^+ S_3^+ S_3^-) \end{aligned} \quad (4.48)$$

As a result of operating on $|aa\beta|$ this gives

$$O |aa\beta| = \frac{1}{\sqrt{2}} [2|aa\beta| - |\alpha\beta\alpha| - |\beta\alpha\alpha|]$$

This is indeed a state of $S = 1/2$, $M_S = 1/2$, however, it is not properly normalized. We must multiply by $3^{-1/2}$ to effect normalization. Let us derive this extra coefficient and set down the rules for the operation of O on any spin-product function with $M_S \neq 0$.

Suppose O operates on a spin-product function with $x\alpha$ spins and $y\beta$ spins and let us assume x is greater than y . First, the constant N in O is to be taken as equal to y . We have $x - y$ excess α spins, hence $M_S = (x - y)/2$. In the sum over i in the operator O the number of choices of i that will give a non-vanishing result is the number of ways of choosing y electrons out of the collection of x electrons, i. e.

$$n = x! / (x - y)! y! \quad (4.49)$$

Operation with O on this spin-product function will produce n states with $S = (x - y)/2$ and $M_S = (x - y)/2$. Thus

$$O \cdot \text{spin-product} = \psi_1 + \psi_2 + \dots + \psi_n = \Phi$$

each of the ψ_i being normalized. We have $(\psi_i, \psi_i) = 1$, $(\psi_i, \psi_j) = \frac{1}{N+1}$. Thus

$$\begin{aligned} (\Phi, \Phi) &= \sum_i (\psi_i, \psi_i) + 2 \sum_{i>j} (\psi_i, \psi_j) \\ &= n(1 + \frac{n-1}{N+1}) \end{aligned}$$

(A SPIN OPERATOR METHOD)

Therefore, if we multiply O by $\left[n(1 + \frac{n-1}{N+1})\right]^{-1/2}$ we will produce a normalized resultant state. We can modify the form of O given in (4.41) so that it can operate on any spin product function. That is

$$O = \frac{1}{(N+1)^{1/2} \left[n(1 + \frac{n-1}{N+1})\right]^{1/2}} \sum_i \left[1 + \sum_{M=1}^N \frac{(-1)^M (N-M)!}{N! M!} \{ (S_{A_i}^- S_{B_i}^+)^M + (S_{A_i}^+ S_{B_i}^-)^M \} \right] \quad (4.50)$$

$$\prod_{j_{A_i}, k_{B_i}}^N (S_{j_{A_i}}^+ S_{j_{A_i}}^- S_{k_{B_i}}^- S_{k_{B_i}}^+ + S_{j_{A_i}}^- S_{j_{A_i}}^+ S_{k_{B_i}}^+ S_{k_{B_i}}^-)$$

This will be taken to be the final form of the operator O . We can write down $\psi_5(S=0)$ directly as

$$\psi_5(S=0) = O [O | \alpha \alpha \beta | \cdot O | \alpha \beta \beta |] \quad (4.51)$$

Before passing on to applications of the operator O other than the creation of the orthogonal singlets for an n electron problem, the beauty of this operator may be further illustrated by writing down the fourteen orthogonal singlets for the eight-electron problem. It is to be recalled that the singlets for the six-electron problem were found by partitioning the six orbitals in the various ways suggested by the branching diagram. The construction of this diagram is not necessary in general and we shall write down the singlets for the eight-electron case without recourse to it. The fourteen orthonormal singlets for the eight-electron problem are:

$$\psi_1(S=0) = O | \alpha \beta | \cdot O | \alpha \beta | \cdot O | \alpha \beta | \cdot | \alpha \beta | \quad (4.52)$$

$$\psi_2(S=0) = O | \alpha \beta | \cdot O | \alpha \alpha \beta \beta | \quad (4.53)$$

$$\psi_3(S=0) = O | \alpha \alpha \beta \beta | \cdot O | \alpha \beta | \quad (4.54)$$

$$\psi_4(S=0) = O | \alpha \alpha \alpha \beta \beta \beta | \quad (4.55)$$

$$\psi_5(S=0) = O | \alpha \beta | \cdot | \alpha \alpha \beta \beta | \cdot O | \alpha \beta | \quad (4.56)$$

$$\psi_6(S=0) = O | \alpha \beta | \cdot O | \alpha \beta | \cdot O | \alpha \alpha \beta \beta | \quad (4.57)$$

$$\psi_7(S=0) = O | \alpha \alpha \beta \beta | \cdot O | \alpha \beta | \cdot O | \alpha \beta | \quad (4.58)$$

$$\psi_8(S=0) = O | \alpha \alpha \beta \beta | \cdot O | \alpha \alpha \beta \beta | \quad (4.59)$$

$$\psi_9(S=0) = O [O | \alpha \alpha \beta \beta | \cdot O | \alpha \beta \beta |] \quad (4.60)$$

(A SPIN OPERATOR METHOD)

$$\psi_{10}(S=0) = O \left[O | \alpha \alpha \beta | \cdot O | \alpha \alpha \beta \beta \beta | \right] \quad (4.61)$$

$$\psi_{11}(S=0) = O \left[O | \alpha \alpha \beta \alpha | \cdot O | \beta \alpha \beta \beta | \right] \quad (4.62)$$

$$\psi_{12}(S=0) = O \left[O | \alpha \alpha \alpha \beta | \cdot O | \alpha \beta \beta \beta | \right] \quad (4.63)$$

$$\psi_{13}(S=0) = O \left[O | \alpha \alpha \beta | \cdot O | \alpha \beta \beta | \right] \cdot O | \alpha \beta | \quad (4.64)$$

$$\psi_{14}(S=0) = O | \alpha \beta | \cdot O \left[O | \alpha \alpha \beta | \cdot O | \alpha \beta \beta | \right] \quad (4.65)$$

Let us now turn from the consideration of how to set up the singlet states and investigate some of the aspects of a configuration interaction calculation. The determination of the expectation value of H with respect to a particular state will be considered first. Suppose we wish to find the expectation value of H with respect to the six-electron singlet given in (4.44) i.e., O .

$$\begin{aligned} (\psi | H | \psi) &= \left[O | \alpha \alpha \alpha \beta \beta \beta | \cdot | H | \cdot O | \alpha \alpha \alpha \beta \beta \beta | \right] \\ &= \left[O A(\alpha \alpha \alpha \beta \beta \beta) | H | O A(\alpha \alpha \alpha \beta \beta \beta) \right] \\ &= \left[A O^2 A(\alpha \alpha \alpha \beta \beta \beta) | H | (\alpha \alpha \alpha \beta \beta \beta) \right] \\ &= \sqrt{N+1} \left[A O(\alpha \alpha \alpha \beta \beta \beta) | H | (\alpha \alpha \alpha \beta \beta \beta) \right] \end{aligned} \quad (4.66)$$

$$(\psi | H | \psi) = 2 A O(\alpha \alpha \alpha \beta \beta \beta) | H | (\alpha \alpha \alpha \beta \beta \beta)$$

The spatial orbitals in the spin-product function $(\alpha \alpha \alpha \beta \beta \beta)$ are assumed to be orthonormal. In the expansion of $A O(\alpha \alpha \alpha \beta \beta \beta)$ the only terms which will make non-zero contributions to the matrix element are those for which a given electron is assigned the same spin on both sides of the matrix element. Therefore, we need only consider those terms in the expansion which lead to $\alpha(1)\alpha(2)\alpha(3)\beta(4)\beta(5)\beta(6)$. Let us write the antisymmetrizing operator as

$$A = \sum_P (-1)^P P^q P^\sigma \quad (4.67)$$

Due to the orthogonality of the spatial orbitals in the spin-product function, the only spatial coordinate permutations in A that will give rise to non-vanishing integrals are the P^q 's which effect a single interchange. When O operates on $(\alpha \alpha \alpha \beta \beta \beta)$, all those values of M in O greater than one cause two or more spin interchanges between sets A and B . Therefore, in order to match spins on both sides of H we will need a permutation from A which is the

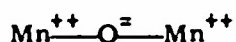
(A SPIN OPERATOR METHOD)

product of at least two interchanges of spin and space coordinates. This will, therefore, lead to a zero contribution due to the spatial orthogonality. Hence the only terms that give contributions from the operator O are those from M values of zero or one. For $M = 0$, we will get non-vanishing integrals from all possible interchanges of a single pair of spatial coordinates within set A or within set B . For $M = 1$ in O the terms arising from the operation of O on the spin-product are all the possible single spin interchanges between sets A and B . Therefore, in order to match spins for a non-zero integral we will need those permutations in A which put the spins back in place. But, these permutations involve the interchange of a single pair of spatial coordinates between sets A and B and will therefore give rise to exchange integrals. Let us now write down $(\Psi|H|\Psi)$.

$$\begin{aligned}
 (\Psi|H|\Psi) = & \left\{ \left[1 - \sum_{j_A=1}^3 \sum_{k_A=1}^3 P_{j_A k_A}^q - \sum_{j_B=4}^6 \sum_{k_B=4}^6 P_{j_B k_B}^q \right. \right. \\
 & \left. \left. + \frac{1}{3} \sum_{j_A=1}^3 \sum_{k_B=4}^6 P_{j_A k_B}^q \right] (\phi_1(1)\alpha(1)\phi_2(2)\alpha(2)\phi_3(3)\alpha(3)\phi_4(4)\beta(4) \right. \\
 & \left. \phi_5(5)\beta(5)\phi_6(6)\beta(6)) |H| (\phi_1(1)\alpha(1)\phi_2(2)\alpha(2) - - - \phi_6(6)\beta(6)) \right\}. \quad (4.68)
 \end{aligned}$$

This expression may seem complicated but the reader will also note that this matrix element is taken with respect to a singlet state which is a linear combination of twenty determinants. This leads to the direct product of twenty determinants and contributions from 180 non-zero cross products.

This general procedure for treating matrix elements can be extended to non-diagonal matrix elements and can be generalized to systems with a rather large number of electrons. The further development of this spin operator method with special emphasis on configuration interaction is now underway. This method is being applied to a configuration interaction investigation of the



model used by Anderson and others on superexchange as an explanation of anti-ferromagnetism. It is hoped that the spin operator method will simplify this problem so that a more rigorous solution can be carried through.

(A SPIN OPERATOR METHOD)

Appendix I

Theorem I

Different paths on the branching diagram terminating at the same destination lead to orthogonal states.

Proof

It is assumed that all spatial orbitals are orthonormal. A one-to-one correspondence exists between a determinant D and spin-product function p and it is $D = Ap$ where A is the antisymmetrizing operator. If two spin-product functions composed of the same set of spatial orbitals differ in the assignment of spin to these spatial orbitals, then the spin-product functions, or the determinants corresponding to them, are orthogonal. It is understood that if two states of the same multiplicity are orthogonal, then the orthogonality is independent of the M_S quantum number of the states. Having made these preliminary remarks, let us proceed.

The first case in the branching diagram where one encounters two different paths leading to the same end-point is for three electrons as shown in Figs. 4-2a and 4-2b. The two states are

$$\begin{aligned}\psi_{2a} &= \frac{1}{\sqrt{2}} \{ |a\beta a| - |a\alpha a| \} = \frac{A}{\sqrt{2}} [(a\beta a) - (a\alpha a)] \\ \psi_{2b} &= \frac{1}{\sqrt{6}} \{ 2|aa\beta| - |a\beta a| - |a\alpha a| \} = \frac{A}{\sqrt{6}} [2(a\alpha\beta) - (a\beta a) - (a\alpha a)]\end{aligned}$$

where $(a\beta a\alpha\beta \dots)$ will in general denote a spin product function. ψ_{2a} and ψ_{2b} are orthogonal.

Let us now consider an arbitrary x -electron terminal point on the branching diagram corresponding to an arbitrary multiplicity, say S . We shall assume that all of the different paths leading to this terminal point correspond to orthogonal states of multiplicity S . It will be shown that all of the states arising from the combination of an additional electron with the various states corresponding to a given terminal point are orthogonal. It will also be shown that any two $(x+1)$ -electron states of the same multiplicity which arise from the combination of the $x+1$ electron with x -electron states of different multiplicities are orthogonal.

Consider the addition of the $x+1$ electron to the i^{th} state corresponding to the x -electron terminal point of multiplicity S which results in an $x+1$ electron state of $S+1/2$ and $M_S = S+1/2$. The composite state is

$$\psi_i(S+1/2, M_S = S+1/2) = \phi_i(S, M_S = S) \cdot \phi(S=1/2, M_S = 1/2)$$

(A SPIN OPERATOR METHOD)

where $\phi(S = 1/2, M_S = 1/2)$ is just $\phi_{x+1}(x+1)\alpha(x+1)$. Now ϕ_i is equal to A_x operating on some linear combination of x -electron spin-product functions where A_x antisymmetrizes a function of x coordinates. $\psi_i(S + 1/2, S + 1/2)$ is equal to A_{x+1} operating on that same linear combination of spin-product functions each spin-product being multiplied by $\phi_{x+1}(x+1)\alpha(x+1)$. Consider any $\psi_j(S + 1/2, S + 1/2)$ for $j \neq i$. This is A_{x+1} operating on the linear combination of spin-product functions corresponding to $\phi_j(S, S)$, each spin-product being multiplied by $\phi_{x+1}(x+1)\alpha(x+1)$. $\psi_i(S, S)$ has been assumed orthogonal to $\psi_j(S, S)$. Therefore, $\psi_i(S + 1/2, S + 1/2)$ is orthogonal to $\psi_j(S + 1/2, S + 1/2)$ for the orthogonality of two linear combinations of x -electron spin-product functions is not changed by multiplying by $\phi_{x+1}(x+1)\alpha(x+1)$ and being operated on by A_{x+1} .

Now consider the addition of the $x + 1$ electron to the i^{th} state corresponding to the x -electron terminal point at multiplicity S and which results in an $x + 1$ electron state $\psi_i(S - 1/2, M_S = S - 1/2)$. We have

$$\psi_i(S - 1/2, M_S = S - 1/2) = C_1 \phi_i(S, S) \phi(1/2, -1/2) + C_2 \phi_i(S, S - 1) \phi(1/2, 1/2)$$

Consider any other $\psi_j(S - 1/2, S - 1/2)$ obtained by adding the $x + 1$ electron to $\phi_j(S, M_S)$. We have

$$\psi_j(S - 1/2, S - 1/2) = C_1 \phi_j(S, S) \phi(1/2, -1/2) + C_2 \phi_j(S, S - 1) \phi(1/2, 1/2)$$

Since $\phi_j(S, S)$ is orthogonal to $\phi_i(S, S)$ and $\phi_j(S, S - 1)$ is orthogonal to $\phi_i(S, S - 1)$, we have that $\psi_i(S - 1/2, S - 1/2)$ is orthogonal to $\psi_j(S - 1/2, S - 1/2)$ by the same arguments given above.

Therefore, it has been shown that all of the states arising from the combination of an additional electron with the various states corresponding to a given terminal point are orthogonal.

Suppose now that we have two $x + 1$ electron states of the same multiplicity which arise from the combination of the $x + 1$ st electron with x -electron states of different multiplicities. Two x -electron states of different multiplicities are orthogonal. Therefore, by proceeding in the same manner as above, it is easily shown that the two $x + 1$ electron states are orthogonal.

Therefore, the theorem is proved.

(A SPIN OPERATOR METHOD)

Appendix II

Theorem II

The spin operator O given in (4.50) commutes with S^2 .

Proof

The operator S^2 may be expressed as

$$S^2 = \text{const.} + \sum_{i>j} P_{ij}^\sigma \quad (\text{A4.1})$$

The commutation of S^2 and O is clearly a question of the commutation of $\sum_{i>j} P_{ij}^\sigma$ and O . It will be established that P_{st}^σ commutes with O for arbitrary s and t and therefore, that S^2 commutes with O . It has been shown that the following properties hold for P_{st}^σ .⁽²⁾

$$S_s^+ P_{st}^\sigma = P_{st}^\sigma S_t^+ \quad (\text{A4.2})$$

$$S_s^- P_{st}^\sigma = P_{st}^\sigma S_t^- \quad (\text{A4.3})$$

$$(S_s^- S_k^+)^M P_{st}^\sigma = P_{st}^\sigma (S_t^- S_k^+)^M \quad (\text{A4.4})$$

$$(S_t^+ S_t^- S_s^+ S_s^-) P_{st}^\sigma = P_{st}^\sigma (S_t^+ S_t^- S_s^+ S_s^-) \quad (\text{A4.5})$$

$$(S_t^+ S_t^- S_k^+ S_k^-) P_{st}^\sigma = P_{st}^\sigma (S_t^+ S_t^- S_k^+ S_k^-) \quad (\text{A4.6})$$

We will speak here about the operation of O on a spin-product function as this allows one to treat the electrons as being distinguishable which is convenient. We can break down the sum over i in the operator O into two cases: (1) All choices of i for which both s and t are in the same group, i.e., A or B . (2) All of those choices of i for which s and t are in different groups, i.e., s in A and t in B . Let us consider case (1). For (A4.5) we have

$$(S_{s_A}^+ S_{s_A}^- S_{t_A}^+ S_{t_A}^-) P_{st}^\sigma = P_{st}^\sigma (S_{s_A}^+ S_{s_A}^- S_{t_A}^+ S_{t_A}^-)$$

The expression $(S_{A_i}^- S_{B_i}^+)^M$ consists of all possible M -tuples, i.e.

$$S_{x1A_i}^- S_{x2A_i}^- \dots S_{xMA_i}^- S_{y1B_i}^+ S_{y2B_i}^+ \dots S_{yMB_i}^+$$

(A SPIN OPERATOR METHOD)

If neither $S_{sA_i}^-$ nor $S_{tA_i}^-$ appear in a given M-tuple, then that M-tuple commutes with P_{st}^σ . If just $S_{sA_i}^-$ appears, then

$$\begin{aligned} & (S_{x1A_i}^- \dots S_{sA_i}^- \dots S_{xMA_i}^- S_{y1B_i}^+ \dots S_{yMB_i}^+) P_{st}^\sigma \\ &= P_{st}^\sigma (S_{x1A_i}^- \dots S_{tA_i}^- \dots S_{xMA_i}^- S_{y1B_i}^+ \dots S_{yMB_i}^+) \end{aligned}$$

Therefore, the sum of the two M-tuples, one with just $S_{sA_i}^-$ and the other with $S_{tA_i}^-$ in place of $S_{sA_i}^-$ but otherwise identical, commutes with P_{st}^σ . Hence P_{st}^σ commutes with the sum of all possible M-tuples which contain either $S_{sA_i}^-$ or $S_{tA_i}^-$ but not both at the same time. If both $S_{sA_i}^-$ and $S_{tA_i}^-$ appear in an M-tuple, then P_{st}^σ commutes with that M-tuple. Therefore, it follows that P_{st}^σ commutes with all O_i in which both s and t are in the same group.

Let us now consider case (2). We can easily show that

$$(S_{sA}^+ S_{sA}^- S_{tB}^- S_{tB}^+) P_{st}^\sigma = P_{st}^\sigma (S_{tA}^+ S_{tA}^- S_{sB}^- S_{sB}^+)$$

Therefore,

$$(S_{sA}^+ S_{sA}^- S_{tB}^- S_{tB}^+ + S_{tA}^+ S_{tA}^- S_{sB}^- S_{sB}^+) P_{st}^\sigma = P_{st}^\sigma (S_{sA}^+ S_{sA}^- S_{tB}^- S_{tB}^+ + S_{tA}^+ S_{tA}^- S_{sB}^- S_{sB}^+)$$

As in case (1) we can examine all of the M-tuples which appear in the expansion of O, those where neither s nor t occur, those where one or the other occur, and those where both s and t appear. In quite the same way as in case (1) it can be shown that P_{st}^σ commutes with the collection of all possible M-tuples.

Therefore, in this fashion one can show that P_{st}^σ commutes with O which implies that S^2 commutes with O.

(A SPIN OPERATOR METHOD)

Appendix III

Theorem III

The spin operator O is hermetian.

Proof

Every term in O appears symmetrically with its hermetian conjugate. Therefore, O is hermetian.

Theorem IV

The spin operator commutes with the Hamiltonian H .

Proof

This is a matter of restricting ourselves to spin-free Hamiltonians.

Theorem V

The spin operator O square is $(N + 1)^{1/2} \left\{ n(1 + \frac{n-1}{N+1}) \right\}^{1/2} O$. (3)

Proof

It will be shown first that $O^2 = \text{const. } O$. The value of the constant will be determined later. We shall consider an N electron problem and the effect of O^2 operating on a single $N \times N$ determinant D_0 , the generalization of O^2 operating on any linear combination of $N \times N$ determinants being trivial.

Let OD_0 be written as

$$OD_0 = C_0 D_0 + C_1 \{ D_1^1 + D_2^1 + \dots + D_X^1 \} \\ + C_2 \{ D_1^2 + D_2^2 + D_3^2 + \dots + \frac{D_X^2(X-1)}{2} \} + \dots + C_X D_X^X$$

where in D_k^j , j refers to the number of reversals in set A or B and k denotes the k^{th} determinant with j reversals. Let us now order these determinants such that

$$D_1^1 = P_{1A1B}^0 D_0, \dots, D_X^1 = P_{XAXB}^0 D_0$$

$$D_1^2 = P_{1A1B}^0 P_{2A2B}^0 D_0, D_2^2 = P_{1A1B}^0 P_{2A3B}^0 D_0 \dots$$

and so forth.

(A SPIN OPERATOR METHOD)

Let us consider $O^2 D_0$ term by term. The first term is just $C_0 OD_0$. The second term may be written

$$C_1 O \{ P_{1A1B}^\sigma + P_{1A2B}^\sigma + \dots + P_{XAXB}^\sigma \} D_0$$

In Appendix II it was shown that any P_{st}^σ commutes with O . Therefore, the second term can be expressed as

$$C_1 \{ P_{1A1B}^\sigma + P_{1A2B}^\sigma + \dots + P_{XAXB}^\sigma \} OD_0$$

We know that OD_0 is an eigenfunction of S^2 which is

$$S^2 = \text{const.} + \sum_{i>j} P_{ij}^\sigma$$

Thus

$$\sum_{i>j} P_{ij}^\sigma (OD_0) = \text{const.} OD_0$$

We can write $\sum_{i>j} P_{ij}^\sigma$ as

$$\sum_{i>j} P_{ij}^\sigma = \sum_{j_A > k_A} P_{j_A k_A}^\sigma + \sum_{j_B > k_B} P_{j_B k_B}^\sigma + \sum_{j_A > k_B} P_{j_A k_B}^\sigma$$

Since $P_{j_A k_A}^\sigma$ and $P_{j_B k_B}^\sigma$ commute with O and since they leave D_0 invariant, we have

$$\sum_{j_A > k_B} P_{j_A k_B}^\sigma (OD_0) = \text{const.} OD_0$$

But, the second term in $O^2 D_0$ is just

$$C_1 \left[\sum_{j_A > k_B} P_{j_A k_B}^\sigma \right] OD_0$$

and is, therefore, a constant times OD_0 .

(A SPIN OPERATOR METHOD)

The third term can be written as

$$C_2 \left[\sum_{j_{A^k B^s A^t B}} \sum P_{j_{A^k B}}^\sigma P_{s_{A^t B}}^\sigma \right] OD_0$$

However, we see from

$$\left[\sum_{j_{A^k B}} P_{j_{A^k B}}^\sigma \right] OD_0 = \text{const. } OD_0$$

that

$$\left[\sum_{j_{A^k B}} P_{j_{A^k B}}^\sigma \right]^2 OD_0 = \left[\sum_{j_{A^k B}} P_{j_{A^k B}}^\sigma \sum_{s_{A^t B}} P_{s_{A^t B}}^\sigma \right] OD_0$$

Hence, the third term in $O^2 D_0$ is just a constant times OD_0 . Proceeding in this manner it is clear that

$$O^2 D_0 = \text{const. } OD_0$$

Now let

$$OD_i = \psi_i$$

We have

$$(\psi_i, \psi_i) = (OD_i, OD_i) = (O^2 D_i, D_i) = \text{const. } (OD_i, D_i) = 1.$$

But,

$$OD_i = \frac{1}{(N+1)^{1/2} \left[n(1 + \frac{n-1}{N+1}) \right]^{1/2}} D_i + \text{orthogonal } D_j \text{'s.}$$

Therefore,

$$\text{const. } (N+1)^{-1/2} \left\{ n(1 + \frac{n-1}{N+1}) \right\}^{-1/2} (D_i, D_i) = 1$$

and

$$\text{const.} = \left[(N+1)^{1/2} \left\{ n(1 + \frac{n-1}{N+1}) \right\}^{1/2} \right]$$

so

$$O^2 = \left[(N+1)^{1/2} \left\{ n(1 + \frac{n-1}{N+1}) \right\}^{1/2} \right] O.$$

Appendix IV

Theorem VI

The spin operator O commutes with the antisymmetrizing operator A .

Proof

The antisymmetrizing operator A can be written as

$$A = \sum_P (-1)^P P^Q P^\sigma$$

where P^Q is a permutation of the spatial coordinates and P^σ is a permutation of the spin coordinates. Any spatial permutation operator clearly commutes with O . Any spin permutation operator can be written as a product of P_{ij}^σ 's. But, any P_{ij}^σ commutes with O . Therefore, any spin permutation operator commutes with O . Hence every permutation in A commutes with O which implies that A commutes with O .

References

1. n is defined in (4.49).
2. P. Dirac, Quantum Mechanics (Oxford, 1947) p 222.
3. See Ref. 1.

G. W. Pratt, Jr.

5. THE WATER MOLECULE

The method being used in the evaluation of integrals involving hydrogen wave functions demands the expansion of the hydrogen 1s wave function about the oxygen nucleus in terms of Legendre polynomials. This expansion is found by differentiating the equation for $e^{-kr'}/r'$, given on Page 51 of the last Quarterly Progress Report, with respect to k . The expansion is written

$$e^{-kr'} = \sum_n (2n+1) P_n(\cos \theta) a_n(kr, ka)$$

where the notation is the same as in the previous Progress Report; a being the O-H distance. The a_n 's (multiplied by r) have been tabulated as a function of a and r .

$$\begin{aligned} r &= 0(.1) 1.2(.2) 4.0(.5) 7(1) 12 \\ a &= 1.4, 1.5, 1.6, 1.8, 2.0, 2.2, 2.6, 3.0, 4.0, \text{ and } 5.0 \\ k &= 1, 2 \\ n &= 0, 1 \end{aligned}$$

Calculations will be made for n up to 5.

We have completed calculation of the hydrogen-oxygen overlap integrals for the values of a mentioned above, as well as the necessary kinetic energy integrals. The calculation of various inter-electronic interaction integrals has been programmed for I.B.M. machines. As yet the program has not been tested.

As was mentioned in the previous Progress Report (Page 13) calculations on the OH molecule are being carried out simultaneously with those for water. The ground state has $^2\Pi_{3/2}$ symmetry. The configurations considered will be listed in a table similar to that of the previous Report. Here s is the oxygen 1s function, σ is the oxygen 2s, p_+ , p_0 , p_- are the three oxygen 2p functions with $m_l = 1, 0, -1$ with respect to the internuclear axis. The hydrogen 1s made orthogonal to s , σ and p_0 we denote by h .

Table 5-1

State	Coefficient	$p_0\alpha$	$p_0\beta$	$p_+\alpha$	$p_+\beta$	$p_-\alpha$	$p_-\beta$	$h\alpha$	$h\beta$	$s\alpha$	$s\beta$	$\sigma\alpha$	$\sigma\beta$
ψ_1		1	2	3	4	5				6	7	8	9
ψ_2		1	2	3				4	5	6	7	8	9
ψ_3				1	2	3		4	5	6	7	8	9
ψ_4	$1/\sqrt{2}$		1	2	3	4		5		6	7	8	9
	$-1/\sqrt{2}$	1		2	3	4			5	6	7	8	9
ψ_5	$2/\sqrt{6}$	1		2	3		4	5		6	7	8	9
	$-1/\sqrt{6}$	1		2	3	4			5	6	7	8	9
	$-1/\sqrt{6}$		1	2	3	4		5		6	7	8	9

(THE WATER MOLECULE)

In Table 5-1 the valence bond state is ψ_4 and the state which goes into the atomic ground state at infinite separation is $\sqrt{3}/2 \psi_4 + 1/2 \psi_5$.

G. F. Koster, H. C. Schweinler

6. SPHERICAL BESSEL FUNCTIONS OF HALF INTEGRAL ORDER AND IMAGINARY ARGUMENT

Calculations of the spherical Bessel functions has been discontinued. The reason for this is the very recent publication of a table of these functions.⁽¹⁾ We have also learned from a private communication of M. P. Barnett that he has completed a more extensive table of these functions. Dr. Barnett has kindly offered to send us his tables on I. B. M. punched cards.

Reference

1. C. W. Jones, A Short Table of the Bessel Functions (Cambridge University Press, Cambridge, 1952)

F. J. Corbató, G. F. Koster, H. C. Schweinler

7. CONFIGURATION INTERACTION APPLIED TO THE HYDROGEN MOLECULE

The addition of a configuration of the form

$$\begin{vmatrix} \sigma_u(1)\alpha(1) & \sigma_u(1)\beta(1) \\ \sigma_u(2)\alpha(2) & \sigma_u(2)\beta(2) \end{vmatrix}$$

with suitable coefficient, to the function

$$\begin{vmatrix} \sigma_g(1)\alpha(1) & \sigma_g(1)\beta(1) \\ \sigma_g(2)\alpha(2) & \sigma_g(2)\beta(2) \end{vmatrix}$$

improves the energy at all internuclear distances, and allows the energy to go to the right value at infinity by removing polar states introduced by the use of molecular orbitals. This process has of course been carried out for the hydrogen molecule using L. C. A. O. 's, and the results are well known. The same procedure is being carried through using M. O. 's slightly more realistic than the L. C. A. O. 's, the solutions of a Hartree equation.

Coulson⁽¹⁾ approximated the σ_g function by the expression

$$\sigma_g = N e^{-0.75\lambda} (1 + a\mu^2 + b\lambda)$$

where λ and μ are the elliptic coordinates

$$\lambda = \frac{r_a + r_b}{R} \quad \mu = \frac{r_a - r_b}{R}$$

Minimization of the energy

$$E_{0g} = \frac{(\sigma_g, H\sigma_g)}{(\sigma_g, \sigma_g)}$$

carried out at $R = 1.4$ a. u. gives the best values of a and b (for the value of R chosen). Coulson found the function to be

$$\sigma_g = 0.83247 e^{-0.75\lambda} (1 + 0.21948\mu^2 - .079575\lambda)$$

and the corresponding binding energy to be 3.535 ev. The observed binding energy is 4.72 ev. Using this σ_g I have set up the Hartree equation

$$\left[-\nabla^2 - \frac{2}{r_a} - \frac{2}{r_b} + \frac{2}{R} + V \right] \psi = \epsilon \psi \quad (7.1)$$

in which V is the average potential energy due to the other electron.

(CONFIGURATION INTERACTION APPLIED TO THE HYDROGEN MOLECULE)

$$V(1) = \frac{1}{(\sigma_g, \sigma_g)} \int \sigma_g^2(2) \frac{2}{r_{12}} d\tau_2$$

The lowest solution of (1) is of course σ_g itself. The next lowest solution, having a nodal plane bisecting the molecular axis, can be approximated by $\sigma_u = N\mu e^{-\delta\lambda}(1 + c\mu^2 + d\lambda \dots)$ adjusting c , d , and δ to minimize the energy in Eq. (7.1).

So far I have determined the average field V , and am now refinding Coulson's value of energy, to check my calculation. This energy is of course one of the two main diagonal elements in the configuration interaction. There still remains the task of finding the best solution with the symmetry σ_u , of Eq. (7.1), and of evaluating the other three matrix elements in the configuration interaction.

Reference

1. C. A. Coulson, Proc. Cambridge Phil. Soc. 34, 204 (1938).

E. Callen

8. NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN THE KCl MOLECULE

Work on the KCl molecule is continuing in the direction outlined in the previous Progress Report. Attention has been directed toward setting up the determinantal wave function for the molecule. The molecular orbitals to be used in the determinant are linear combinations of atomic orbitals and the procedure for choosing the coefficients follows that given by Roothaan.⁽¹⁾ Polarization is included by appropriate distortion of the K^+ and Cl^- atomic orbitals. Several methods of doing this are being studied. In particular the form:

$$\psi = \psi_{nlm}^0 (1 + r^\nu Y_{l'}^{m'})$$

where

ψ_{nlm}^0 = unperturbed one-electron atomic function

r = distance from nucleus to electron

ν = variation parameter

$$Y_{l'}^{m'} = \text{surface spherical harmonic} = \frac{(-1)^{m'}}{\sqrt{2\pi}} \left[\frac{2l' + 1}{2} \frac{(l' - m')!}{(l' + m')!} \right]^{1/2} P_{l'}^{m'}(\cos \theta) e^{im'\phi}$$

is being investigated.

Reference

1. C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).

L. C. Allen

9. CONFIGURATION INTERACTION IN THE HYDROGEN FLUORIDE MOLECULE

The numerical calculations required for the configuration interaction treatment of the hydrogen fluoride molecule described in the last Progress Report are being carried out. These calculations were recently set back several weeks by the discovery of a number of numerical errors in the calculated coefficients of the expansion of the hydrogen 1s orbital about the fluorine nucleus.

The calculation of the energy at the experimental equilibrium H-F distance is expected to be completed shortly, and the complete set of results should be available by the time of the next Progress Report.

R. E. Merrifield

10. CONFIGURATION INTERACTION FOR THE FLUORINE MOLECULE⁽¹⁾

The method of configuration interaction is being applied to F_2 in order to study its energy levels and wave functions. The procedure being used is outlined below. Slater⁽²⁾ has discussed some aspects of the problem in more detail than is given here.

One-electron molecular orbitals are formed by making linear combinations of the atomic orbitals for the two atoms. The atomic orbitals being used are the $1s$, $2s$, $2p_+$, $2p_0$, and $2p_-$. The subscripts $+$, 0 , $-$ denote $+1$, 0 , -1 units of orbital angular momentum about the molecular axis. The space parts of the orbitals are made up as symmetrical or antisymmetrical combinations of two corresponding atomic orbitals on the two atoms plus small amounts of the other orbitals in order to make the molecular orbitals orthogonal. Actually the simple symmetrical and antisymmetrical combinations are orthogonal except within two small groups. These groups are the symmetrical combinations made of $1s$, $2s$, and $2p_0$ functions and the antisymmetrical combinations made of $1s$, $2s$, and $2p_0$ functions. Orthogonal combinations are formed in these two groups by a Schmidt orthogonalization process. In the symmetrical (or antisymmetrical) group the molecular orbital made of $1s$ functions is taken as the first combination. A second combination is formed from the $2s$ functions and small amounts of the $1s$ functions in such a way as to be orthogonal to the first combination. The third combination is formed from the $2p_0$ functions and small amounts of the $1s$ and $2s$ functions in such a way as to make this combination orthogonal to the first two.

These orthogonal molecular orbitals are labeled in the following manner. Odd numbered orbitals will be the product of a space function and an α spin function; even numbered orbitals, of a space function and a β spin function. The numbers corresponding to the space parts of the orbitals are associated with the type of atomic orbital which is most important in the various molecular orbitals. Molecular orbitals 1 and 2 are associated with the $1s_a + 1s_b$ combination; 3 and 4, $1s_a - 1s_b$; 5 and 6, $2s_a + 2s_b$; 7 and 8, $2s_a - 2s_b$; 9 and 10, $2p_{+a} + 2p_{+b}$; 11 and 12, $2p_{+a} - 2p_{+b}$; 13 and 14, $2p_{0a} + 2p_{0b}$; 15 and 16, $2p_{0a} - 2p_{0b}$; 17 and 18, $2p_{-a} + 2p_{-b}$; 19 and 20, $2p_{-a} - 2p_{-b}$. The subscripts a and b designate the two atoms of the molecule.

The configurations which will be considered in the present treatment will be only those in which molecular orbitals 1 - 8, formed from the $1s$ and $2s$ atomic functions, are always filled. It is being assumed that orbitals 9 - 20 lie enough higher in energy than orbitals 1 - 8 that the interaction between these two sets of orbitals can be neglected. The number of electrons in the molecule is 18, so that all but two orbitals are filled. The number of configurations to be considered then is 66. The wave function for a configuration is the determinantal function which makes an antisymmetrical wave function from the 18 orbitals of the configuration. For simplicity the configurations will be designated by the symbol (i, j) , where i and j are the two orbitals not included in the configuration.

The number of configurations which must be considered can be further reduced by considering symmetry properties. Only wave functions of a given symmetry will have matrix elements or react with each other. In some cases it will be necessary to form linear combina-

(CONFIGURATION INTERACTION FOR THE FLUORINE MOLECULE)

tions of configurations in order to have functions of a given symmetry. The ground state wave function is known to have $^1\sum_g^+$ symmetry.⁽³⁾ The \sum signifies that such a function has zero orbital angular momentum about the molecular axis. The superscript 1 signifies that the function is a singlet spin state. The superscript + indicates that the function goes into itself when the coordinates of all electrons are reflected in a plane passing through the axis of the molecule. And the subscript g indicates that the function goes into itself when the coordinates of all electrons are reflected in the midpoint of the molecule.

The number of states having $^1\sum_g^+$ symmetry is only 4. These states are given in Table 10-1. Each row of the table represents a state. For a state each number in the row is the coefficient of the configuration at the head of its column. The coefficients are chosen so that each state is normalized if the configurations are normalized.

Table 10-1
Table of $^1\sum_g^+$ States

State No.	(13, 14)	(15, 16)	(9, 18)	(10, 17)	(11, 20)	(12, 19)
1	1	0	0	0	0	0
2	0	1	0	0	0	0
3	0	0	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	0
4	0	0	0	0	$1/\sqrt{2}$	$-1/\sqrt{2}$

Work is now proceeding on calculation of the matrix elements of energy between the various states. These matrix elements can be expressed in terms of one- and two-electron integrals involving the various atomic orbitals on the two atoms. Hartree-Fock atomic orbitals⁽⁴⁾ will be used in evaluating these integrals.

References

1. The author is the holder of a Lilly Postdoctoral Fellowship from the National Research Council.
2. J. C. Slater, Technical Report No. 3, Solid-State and Molecular Theory Group, M.I.T., February 15, 1953, pp. 124-141, especially pp. 140-141.
3. G. Herzberg, Spectra of Diatomic Molecules, 2nd Edition (D. Van Nostrand, New York) 1950, p. 343.
4. F. W. Brown, Phys. Rev. 44, 214 (1933).

J. H. Barrett

11. THE CARBON -- CARBON BOND IN ETHANE

The investigation just begun on the ethane molecule is in no sense as complete a job as some of the other molecular studies of this Group. It is to be a quantitative test of the prevalent idea of independence of bonds in molecules, in particular the covalent carbon-carbon bond. There seems to be a valid concept of a carbon-carbon bond which appears with distinctive energy and internuclear distance in different molecules, the differences being in the complexes attached onto the "outside" of the carbon atoms. In ethane, each carbon is part of a methyl group, an equilateral triangle of hydrogen atoms with the carbon at the apex of the tetrahedron. The complete ethane molecule has the tetrahedrons apex to apex.

The ground state spatial configuration is most likely the one in which the two hydrogen triangles are at angle of 60° to each other. Their superposition would appear as a six-pointed star and this arrangement is called "staggered". The "eclipsed" arrangement in which there are three colinear pairs of hydrogen atoms probably lies higher in energy than the staggered. We intend to treat both geometric configurations and we shall indicate the proposed extent of the calculation with the case of staggered ethane. The electronic configurations to be discussed are those suggested by Professor Slater in a Technical Report of this Group.⁽¹⁾

Electrons shall be assigned to molecular orbitals formed as linear combinations of atomic orbitals. The atomic orbitals to be used are the 2s and 2p on the carbons and the 1s on the hydrogens, a total of 14 space orbitals with 14 electrons to be assigned. (Consider the carbon 1s functions as strictly atomic and filled.) The symmetry orbitals to be formed will be ones of definite parity and proper behavior under a 120° rotation about the carbon-carbon axis. There is another type of symmetry operation, that of reflection in any of the three axial planes containing the perpendicular bisectors of the hydrogen triangles and this type of operation is to be included in forming the ground state as a totally symmetric singlet state.

From each hydrogen group there can be formed a combination which transforms into itself multiplied by $e^{2\pi i/3}$ under the 120° rotation, a combination which is multiplied by $e^{-2\pi i/3}$ and one which is transformed precisely into itself. Let these functions be denoted by h_+ , h_- , and h_0 , respectively. The p_+ orbitals of the carbons are to be combined with the h_+ 's to yield two gerade and two ungerade molecular orbitals. For each parity one orbital can be considered bonding and one anti-bonding. That is, the bonding orbital will have the larger charge concentration between the carbon and the hydrogens in the methyl complex. We shall fill the bonding g orbital and the bonding u orbital. Similarly for the p_- and h_- combinations. This takes care of 8 electrons.

The h_0 orbitals and the 2s and $2p_0$ carbon orbitals are to be combined. There will be three g and three u molecular orbitals. Two of each parity will be mainly 2s and h_0 again to be separated into bonding and anti-bonding insofar as carbon-hydrogen interaction is concerned. Fill the bonding g and the bonding u leaving two electrons to be distributed among the two remaining molecular orbitals, both mainly $2p_0$, one g and one u. At this point we shall allow configuration interaction. Both electrons can go into the g or both can go into the u. These two configurations can interact and must interact to allow the proper dissocia-

(THE CARBON -- CARBON BOND IN ETHANE)

tion of the carbon-carbon bond.

This is limited configuration interaction so that the coefficients in the linear combinations of atomic orbitals must be energetically optimum. There is one independent variable associated with the two g combinations of the p_+ and h_+ orbitals and one independent variable associated with the u combinations. (The $-$ orbitals make use of the same orthogonalization procedure.) There are three independent variables associated with the g combinations of the h_o , $2s$, and $2p_o$ orbitals and three for the u combinations. The ground state energy, resulting from the interaction of two configurations, is to be minimized by the choice of these eight variables.

Reference

1. I. C. Slater, Technical Report No. 3, Solid-State and Molecular Theory Group, M.I.T. February 15, 1953.

A. Meckler

Errata

In the October 15, 1952 Progress Report there appeared a slightly wrong formula for the dissociation energy, and consequently, the table of molecular parameters was in error. The corrections are:

$$D_o = A + a\sqrt{\frac{D}{\mu}} - \frac{a^2}{4\mu}$$

$$\omega_e = 2a\sqrt{\frac{D}{\mu}}$$

Table 4-1

	Parameter	Experimental	Calculated
$^3\Sigma_g^-$	R_o	2.28	2.255
	D_o	-.3735	-.3660
	$\omega_e(\text{cm}^{-1})$	1580.4	1514.3
$^1\Sigma_g^+$	R_o	2.32	2.30
	D_o	-.2527	-.2051
	$\omega_e(\text{cm}^{-1})$	1432.7	1272.9

12. LIMITED CONFIGURATION INTERACTION TREATMENT OF THE NH_3 MOLECULE

Work on the S_8 molecule mentioned in the last Progress Report has ceased because it was felt that the extremely large amount of calculation necessary to complete a reasonably plausible molecular orbital treatment of the molecule was not warranted in view of the very limited significance of such a model.

An investigation of the ground state of the NH_3 molecule has been started. From the 3003 determinantal wave functions obtained by using 1s, 2s, and 2p one-electron functions for the nitrogen atom, and 1s functions for each of the hydrogen atoms, and always keeping the 1s nitrogen state filled, 98 molecular wave functions can be formed which are completely symmetric under the group of operations defined by the atomic nuclei (C_{3v}) and which are singlets. The ground state of NH_3 is of this type (denoted by $^1\text{A}_1$).

It is clearly not practicable to do a complete configuration interaction between these 98 configurations. Some relatively small number of more important ones must be selected and it is the purpose of the present project to carry out the configuration interaction with a selection of this nature. The final results will thus be a test of the method of selection.

For ease in computation it is desirable to build up the necessary determinants from orthogonal one-electron functions. However just this choice makes the selection of a small number of configurations difficult since previous work^(1, 2) indicates that a large number of configurations built up in this manner are necessary for a good description of the ground state of a molecule. The alternative method of using non-orthogonal one-electron functions makes the selection of a small number of important configurations simple and this method has been exploited by several authors.⁽³⁾ However, the good results obtained from these calculations are rendered suspect by an improper treatment of non-orthogonality and the evaluation of many integrals from experimental information and the authors themselves are the first to admit that the rigorous application of their method is not feasible.

A plausible method of selection, suggested by Slater,⁽⁴⁾ which will be used in our calculation is based on the observation that the molecular orbitals for a molecule such as NH_3 can be qualitatively divided into three groups: one group of three in which the charge is concentrated between the hydrogens and the nitrogen, representing bonding; a second group of three in which there is a node between the hydrogens and the nitrogen, representing anti-bonding; and a third group of one which is not directly concerned in the bonding. One way of representing these functions is as the equivalent orbitals of Lennard-Jones.⁽⁵⁾ The molecular orbital state, which is the best one-determinant wave function composed of orthogonal one-electron functions at internuclear distances usually found in molecules, consists in filling groups one and three completely and leaving group two empty. The proposed method of selection consists in always filling set three but allowing one or two of the electrons in one, two, or three of the "bonding" orbitals to be excited to the corresponding "antibonding" orbitals. However we always keep two electrons in each "bond". The treatment thus proposes that it is not likely for one "bond" to be lacking an electron while another "bond" has an excess electron. The final result is 13 configurations with $^1\text{A}_1$ symmetry. This limited selec-

(LIMITED CONFIGURATION INTERACTION TREATMENT OF THE NH_3 MOLECULE

tion of configurations is a great improvement over the molecular orbital state because it can reduce to a non-ionized state of the nitrogen atom at infinite separation. This should have the effect of improving the surface of energy versus internuclear separations in the region of separations greater than the equilibrium distances, a region where the molecular orbital solution is notoriously poor.

The matrix elements of the 13×13 secular equation are now being set up. It is planned to evaluate the various two-electron integrals occurring in these matrix elements by the machine methods of Koster and Schweinler.⁽⁶⁾

References

1. J. C. Slater, J. Chem. Phys. 19, 220 (1951).
2. A. Meckler, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1952, p. 62.
3. Both M. Kotani and M. Siga, Proc. Phys.-Math. Soc. Japan 19, 471 (1937) and H. H. Voge, J. Chem. Phys. 4, 581 (1936) treated CH_4 this way and recently T. Itoh, K. Ohno and M. Kotani, J. Phys. Soc. Japan 8, 41 (1953) have done a similar treatment of the CH_3 radical.
4. J. C. Slater, Technical Report No. 3, Solid-State and Molecular Theory Group, M.I.T., February 15, 1953.
5. J. E. Lennard-Jones, Proc. Roy. Soc. (London) A198, 1, 14 (1949).
6. G. Koster and H. C. Schweinler, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1953, p. 11.

H. Kaplan

13. A STUDY OF $2Z_p$ IN ATOMS

The calculations of $2Z_p$, the effective nuclear charge for the potential in an atom, have been completed. Using the method outlined in a previous Progress Report, ⁽¹⁾ the total (normalized) radial wave function and $2Z_p$ have been obtained for those atoms treated by the Hartree, Hartree-Fock, or Slater self-consistent field methods. ⁽²⁾ Table 13-1 lists the atoms for which $2Z_p$ has been obtained in this way, together with those atoms whose $2Z_p$'s are available in the literature. The Table gives a complete picture of all the available potentials in atoms.

Table 13-1
Degree of Ionization

Atomic Number	0	+1	+2	+3	+4
2	He*				
3		Li*			
4	Be*		Be*		
5	B				
6	C		C		C
7	N				
8	O	O	O	O	
9	F*				
10	Ne*				
11	Na*	Na			
12			Mg		
13		Al*	Al	Al*	
14			Si*	Si	Si
18	Ar*				
19	K	K*	K*		
20	Ca*	Ca	Ca*		
24	Cr		Cr ⁺⁺		
26	Fe*				
29		Cu*			
30	Zn				
31	Ga	Ga		Ga	
32	Ge		Ge		
33	As	As	As	As	
34		Rb*			
37		Ag*			

(A STUDY OF $2Z_p$ IN ATOMS)

Table 13-1 (con'd)

Atomic Number	0	+ 1	+ 2	+ 3	+ 4
55		Cs*			
74	W*				
80	Hg*		Hg*		

*Available in the literature.

References

1. Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1952, p. 26.
2. H. H. Landolt and R. Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, 6 Auflage, I. Band (Springer, Berlin) 1950, p. 276, gives a complete listing.

A. J. Freeman

14. ORBITAL EFFECT IN NEUTRON-ELECTRON MAGNETIC SCATTERING

The spin-spin part (\mathcal{H}_{SS}) of the neutron-electron magnetic interaction has been considered in some detail in the literature,⁽¹⁾ while the spin-orbit part (\mathcal{H}_{SL}), associated with the interaction between the neutron magnetic moment and a moving electron, has not. It is worthwhile to consider both of these in detail from the viewpoint of exploiting the scattering of thermal neutrons from magnetic materials as a tool for investigating the electronic structure of matter.

The magnetic Hamiltonian is

$$\mathcal{H}_{SS} + \mathcal{H}_{SL} = -\vec{\mu}_n \cdot \vec{H}^{(S)} - \vec{\mu}_n \cdot \vec{H}^{(L)} \quad (15.1)$$

in which $\vec{\mu}_n = g_n(m/M_p) \beta \vec{s}_n$ is the neutron magnetic moment, and the magnetic field at the neutron generated by electrons of the scatterer is given by

$$\vec{H}^{(S)} = \sum_j -\nabla_j \times [\vec{\mu}_j \times (\nabla_j r_{nj}^{-1})] \quad (15.2)$$

$$\vec{H}^{(L)} = \frac{e}{mc} \sum_j (\nabla_j r_{nj}^{-1}) \times \vec{p}_j \quad (15.3)$$

where $\vec{\mu}_j = -2\beta\vec{s}_j$ is the magnetic moment, \vec{r}_j the position, \vec{p}_j the momentum, and \vec{s}_j the spin angular momentum (in units of \hbar) of the j^{th} electron, the summation being over all electrons; \vec{r}_n is the position, \vec{s}_n the spin, and $g_n = -3.83$ the g -factor of the neutron; m/M_p is the electron-proton mass ratio; $\beta = e\hbar/2mc$ is the Bohr magneton; $r_{nj} = |\vec{r}_n - \vec{r}_j|$. These expressions for \mathcal{H}_{SS} and \mathcal{H}_{SL} were obtained by transcribing the nonrelativistic form of the Breit fine structure Hamiltonian⁽²⁾ for the electromagnetic interaction between two electrons to apply to the interaction between a neutron and an electron, neglecting a term in the neutron momentum \vec{p}_n , smaller by a factor $\sim m/M_p$ than the electron momentum term in (15.3). Eq. (15.2), when expanded, includes besides the usual dipolar energy a δ -function term necessary to obtain agreement with experiment.⁽³⁾ Both (15.2) and (15.3) may be derived in an elementary way from classical electromagnetic theory.

Consider the differential scattering cross section in center-of-mass coordinates in Born approximation for the scattering of a monochromatic beam of neutrons by a molecule or small crystal. The Born approximation is expected to be valid here for scatterers of linear dimensions less than about 20A independent of neutron wavelength, but may well be valid for much larger scatterers. The matrix elements of (15.1) involved are between wave functions of the system neutron plus scatterer with no interaction. When integration is carried out over the neutron space and spin coordinates, and an average over initial neutron spin states is performed, the differential cross section may be written

(ORBITAL EFFECT IN NEUTRON-ELECTRON MAGNETIC SCATTERING)

$$\sigma(\omega) = \left(R \frac{g_n e^2}{2mc^2} \right)^2 \sum_b \frac{k_b}{k_a} \left\{ \left[\bar{I} - \vec{e}_{ba} \vec{e}_{ba} \right] : \left[\vec{P}_{ab}^S \vec{P}_{ba}^S - i(\vec{P}_{ab}^S \vec{P}_{ba}^L + \vec{P}_{ab}^L \vec{P}_{ba}^S) \right] - \vec{P}_{ab}^L \cdot \vec{P}_{ba}^L \right\}, \quad (15.4)$$

corresponding to an unpolarized incident beam. In (15.4) we have used the abbreviation

$$\vec{P}_{ba} = \int \psi_b^* \vec{P}(\vec{K}_{ba}) \psi_a d\tau \quad (15.5)$$

for matrix elements of the operators

$$\vec{P}^{(S)}(\vec{K}) = \sum_j \exp[i\vec{K} \cdot \vec{r}_j] \vec{s}_j \quad (15.6)$$

$$\vec{P}^{(L)}(\vec{K}) = \sum_j \exp[i\vec{K} \cdot \vec{r}_j] K^{-2} \vec{K} \times (\vec{p}_j/\hbar) \quad (15.7)$$

with respect to wave functions ψ of the scatterer. The subscripts a and b refer, respectively, to initial and final states; R is the ratio of the reduced mass to the proton mass; \vec{k} is the neutron wave vector, $\vec{K}_{ba} = \vec{k}_a - \vec{k}_b = K_{ba} \vec{e}_{ba}$; \bar{I} is the unit dyadic; k_a and k_b are related by conservation of energy.

Eq. (15.4), or analogous expressions for cases in which the incident neutron beam is polarized and/or the scattered beam is analyzed, should be useful for testing electronic wave functions of a magnetic scatterer, especially in regions frequented by valence electrons. Assuming that any bound-state electronic eigenfunction of the scatterer can be expressed as a linear combination of antisymmetrized products of orthonormal one-electron orbitals ϕ , e.g., molecular or crystal orbitals, the electronic part of the matrix elements (15.5) is expressible as a linear combination of one-electron matrix elements of the types

$$(\phi' | \exp[i\vec{K} \cdot \vec{r}] | \phi) \quad (15.8)$$

$$(\phi' | \exp[i\vec{K} \cdot \vec{r}] \nabla | \phi). \quad (15.9)$$

The ϕ 's are commonly approximated as a linear combination of orthonormal atomic orbitals⁽⁴⁾ $u_n(\vec{r}) Y^m(\theta, \phi) \chi_{m_s}(\sigma)$, in which case (15.5) is ultimately expressible as a linear combination of matrix elements (15.8) and (15.9) in which the ϕ 's are atomic orbitals about the same center. These can be evaluated quite generally except for radial integrals:

$$(n'l'm'm_s' | \exp[i\vec{K} \cdot \vec{r}] \vec{s} | n'l'm m_s) = (m_s' | \vec{s} | m_s) \int_0^\infty u_{n'l'}(l'm') \exp[i\vec{K} \cdot \vec{r}] l m u_{nl} r^2 dr,$$

(ORBITAL EFFECT IN NEUTRON-ELECTRON MAGNETIC SCATTERING)

$$(n'l'm'm'_s | \exp[i\vec{K} \cdot \vec{r}] \nabla | nlm m_s) = \delta_{m'_s m_s} \int_0^\infty u_{n'l'} \times (l'm' | \exp[i\vec{K} \cdot \vec{r}] \nabla | lm) u_{nl} r^2 dr,$$

in which the angular matrix elements $(l'm' | \exp[i\vec{K} \cdot \vec{r}] | lm)$ and $(l'm' | \exp[i\vec{K} \cdot \vec{r}] \nabla | lm)$ involve linear combinations of spherical Bessel functions $j_p(Kr)$ with coefficients depending on the direction of \vec{K} times 1, $1/r$, or $\partial/\partial r$; tables of these matrix elements for l' , $l \leq 3$ will be published elsewhere.

For free atomic scatterers, closed shells yield no contribution to (15.4) and, if spin interactions are neglected in the atomic Hamiltonian, neither do the cross-terms in (15.4).

References

1. For example, O. Halpern and M. H. Johnson, Phys. Rev. 55, 898 (1939); G. T. Trammell, Cambridge A. P. S. meeting, January, 1953, Abstract J3.
2. G. Breit, Phys. Rev. 34, 553 (1929).
3. C. G. Shull, E. O. Wollan, and W. A. Strauser, Phys. Rev. 81, 483 (1951).
4. See, for example, E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge) 1951.

W. H. Kleiner

15. ADSORBED SURFACE LAYERS ON SEMICONDUCTORS

Investigations have been started on the behavior of adsorbed surface layers on semiconductors. The purpose of this investigation is to predict the energy spectrum which arises from the surface in connection with the adsorbed layers. A discussion of that problem seems to be promising since from the interpretation of new experimental material⁽¹⁾ a more detailed picture of the surface has been obtained.

Reference

1. W. H. Brattain and J. Bardeen, Bell System Tech. J. XXXII, 1 (1953).

H. Statz

16. CONNECTION BETWEEN THE MANY-ELECTRON INTERACTION AND THE ONE-ELECTRON PERIODIC POTENTIAL PROBLEMS

The extension of Tomonaga's⁽¹⁾ collective coordinate model of a one-dimensional system of interacting electrons without spin (based on Bloch's classical approach in terms of "sound waves") to include the effect of an external periodic potential, as proposed in the previous Progress Report, has been effected.

Using the language of second quantization, Tomonaga has expressed the Hamiltonian in terms of the Fourier components of the density, which are shown to approximately satisfy the commutation relations characteristic of a Bose-Einstein or phonon field. Since the Hamiltonian is solely a bilinear function of these Fourier density components, or collective coordinates, it is then relatively simple to rotate the Hamiltonian into a diagonal form, representing a collection of uncoupled sound quanta or phonons, by a straightforward canonical transformation which Tomonaga exhibits. To extend this rotation (in Hilbert space) to include the periodic potential term, it is simply necessary to displace the origins of the rotated canonical set of (real) variables given by Tomonaga as follows:

$$p_n' = p_n + \left[\frac{i(V_n - V_n^*) \sqrt{\frac{|n|}{2}}}{T_n^{1/4} (T_n + 2U_n)^{3/4}} \right]$$

$$q_n' = q_n + \left[\frac{(V_n + V_n^*) \sqrt{\frac{|n|}{2}}}{T_n^{1/4} (T_n + 2U_n)^{3/4}} \right]$$

where N is the number of electrons.

n is the index of the Fourier components, which correspond to an arbitrary (large) unit of periodicity of length L .

V_n is the Fourier component of the external periodic potential V (many of the V_n will be zero if the period of V is comparable to the average interparticle distance rather than L).

$T_n = \left[\frac{1}{2m} \left(\frac{h}{L} \right)^2 \right] (N - 1) |n|$ is the Fourier component of the kinetic energy.

$U_n = |n| J_n$, where J_n is the Fourier component of the Coulomb potential ($J_n \sim 1/n^2$).

The part of the final Hamiltonian representing the excited states of the system, and thus yielding the dispersion relation, is not affected by the above shift in origin, and we shall not consider excited states further. In the final ground state Hamiltonian we find the effect of the periodic potential to be represented by the term:

$$- \sum_{|n| \leq \frac{N-1}{4}} \frac{|n| |V_n|^2}{(T_n + 2U_n)}$$

(MANY-ELECTRON INTERACTION AND ONE-ELECTRON PERIODIC POTENTIAL)

The restriction on $|n|$, or the size of the reciprocal vector, is common to all terms, and expresses the inherent limitation of the method to cases where sound quanta of smaller wavelength -- and hence events or forces of shorter range -- do not occur and where excited holes and electrons are not further away than this maximum n in momentum space from the level of the Fermi sea. The derivative of this term with respect to N should give the one-electron energy due to the periodic potential of the highest electron in the Fermi sea: no discontinuity is observed corresponding to an energy gap, presumably because the complete description of the perturbation effect of the periodic potential requires the use of sound quanta of smaller wavelength than are allowed by this method.

On the one-electron picture the effect of the periodic potential may be estimated from second order perturbation theory:

$$\Delta E = \sum_{j \neq i} \frac{|V_{ij}|^2}{\frac{p_i^2}{2m} - \frac{p_j^2}{2m}}.$$

Energy gaps are obtained by solving a degeneracy problem for $|p_i|^2 = |p_j|^2$, not by second order perturbation theory, but we note that the effects of the gap are equal and opposite on the energies of the electron just below and on that just above the gap. Hence if we sum these ΔE for all the electrons in the Fermi sea, we should obtain a correct expression for the total effect on energy of the periodic potential to check the one we have found by the Tomonaga method:

$$\begin{aligned} \Delta E(\text{total lattice}) &= \sum_{|i| \leq \frac{N}{2}} \sum_{j \neq i} \frac{|V_{ij}|^2}{E_i^0 - E_j^0} \\ &= - \sum_{n \neq 0} \frac{|V_n|^2}{\left[\frac{1}{2m} \left(\frac{h}{L} \right)^2 \right] 2n} \sum_{\substack{i=0 \\ i \neq -\frac{n}{2}}}^{N-1/2} \frac{1}{i + \frac{n}{2}} \\ &\doteq - \sum_{n \neq 0} \frac{|V_n|^2}{\left[\frac{1}{2m} \left(\frac{h}{L} \right)^2 \right] 2n} \log \left(\frac{1 + \frac{n}{N-1}}{1 - \frac{n}{N-1}} \right) \end{aligned}$$

or other forms depending on the size of n relative to N . Expanding, we at once check the form derived above if we note that $U_n = 0$ in this one-electron approximation:

$$\Delta E(\text{total lattice}) \doteq - \sum_{\substack{n \neq 0 \\ |n| \leq \frac{N-1}{4}}} \frac{V_n^2}{\left[\frac{1}{2m} \left(\frac{h}{L} \right)^2 \right] 2n} \left[2 \frac{n}{N-1} \right] = - \sum_{n \neq 0} \frac{|n| \leq \frac{N-1}{4}}{\frac{4}{N-1}} \frac{|V_n|^2 |n|}{T_n}$$

(MANY-ELECTRON INTERACTION AND ONE-ELECTRON PERIODIC POTENTIAL)

where the terms omitted in the sum, plus the other errors, are small if the conditions required for the validity of Tomonaga's method are satisfied; in particular, if V_n is small for n larger than $\frac{N-1}{4}$ (as well as zero for all n not multiples of the fundamental n_0 corresponding to the period of V , in general different from L). For comparison we may expand the Coulomb interaction energy expression for the ground state as given in Tomonaga; ⁽¹⁾ we obtain as the leading terms in U_n/T_n

$$\frac{1}{2} N^2 J_0 + \frac{1}{2} \sum_{n \neq 0} |n| J_n - \frac{1}{4} \sum_{n \neq 0} \frac{n^2 J_n}{T_n}$$

with $|n| < \frac{N-1}{4}$ as usual.

Inasmuch as we are in a Heisenberg, or operator, representation and cannot easily obtain the wave functions in the original coordinates, it was decided to first investigate the effect of the periodic potential transformation on the correlation in position of the electrons. Extending the correlation expression given by Tomonaga to include the periodic potential effect, we find for the probability in the ground state of a certain electron being in a unit length at a distance ξ from a certain other electron

$$C(\xi) = \frac{1}{L} \left\{ 1 + \frac{2}{N} \sum_{n>0} \left(1 - \frac{U_n}{T_n} \right) \frac{n}{N} \cos \left(2\pi \frac{\xi}{L} \frac{n}{N} \right) + 8 \sum_{n>0} \left(1 - 4 \frac{U_n}{T_n} \right) \left(\frac{n}{N} \right)^2 \left(\frac{V_n}{T_n} \right)^2 \cos \left(2\pi \frac{\xi}{L} \frac{n}{N} \right) \right\}$$

as an approximate form for $U_n/T_n \ll 1$, where $l = L/N$ is the average interparticle distance. We observe that a factor of four differentiates the effect of the Coulomb interaction on the correlation due to the exclusion principle from the effect on the correlation due to the periodic potential. However, we must not attach too much importance to expansions in terms of U_n/T_n since the advantage of Tomonaga's method over perturbation theory is precisely that U_n does not have to be small for small n . Further we must cut off the above sums at $|n| = \frac{N-1}{4}$ as usual; but here this cutoff is arbitrary since even the closed form of $C(\xi)$ (not given here) becomes indeterminate but large if the summation is extended indefinitely, while in the summation for the ground state (but not excited state) energy the tail of the summation is inherently small.

For large L we may approximate the above sum accurately by an integral. Let us consider the special case of a non-interacting, free electron gas ($U_n = V_n = 0$); we may easily perform the integration to obtain:

$$C(\xi) = \frac{1}{L} \left\{ 1 - \left[2 \frac{\sin^2 \left(\frac{\pi}{4} \frac{\xi}{l} \right)}{\pi^2 \left(\frac{\xi}{l} \right)^2} - \frac{\sin \left(\frac{\pi}{2} \frac{\xi}{l} \right)}{2\pi \left(\frac{\xi}{l} \right)} \right] \right\}.$$

If for comparison we determine this Pauli Exclusion Principle correlation by direct integration

(MANY-ELECTRON INTERACTION AND ONE-ELECTRON PERIODIC POTENTIAL)

over the product of two determinants of exponential one-electron wave functions, we find

$$C(\xi) = \frac{1}{L} \left\{ 1 - \left[\frac{\sin^2(\pi \frac{\xi}{L})}{\pi^2 (\frac{\xi}{L})^2} \right] \right\}$$

for this free-electron, one-dimensional case, following the approach of Wigner and Seitz.⁽²⁾ Since spin is not included in our formulation, this case corresponds to the parallel spin case in a real electron gas as far as the exclusion principle is concerned. Clearly the two expressions disagree.

If we multiply $C(\xi)$ by N we obtain the probability of any electron being in a unit length at a distance ξ from the fixed one; i.e., simply a density expression. Clearly the first term in each of the above expressions then corresponds to the constant average density, while the second term gives the "exchange charge density" in the language of Wigner and Seitz: $NC(\xi) = \rho_0 - \rho_x$. Although the general natures of these exchange charge densities are similar, the Tomonaga expression has an $(\xi/L)^{-1}$ average behavior for the large (ξ/L) where it is presumed most valid, while the correct Wigner-Seitz expression has a $(\xi/L)^{-2}$ behavior. As (ξ/L) goes to zero, the Tomonaga exchange charge density actually becomes negative, while the Wigner-Seitz zero value exactly cancels the constant ρ_0 as it should. Finally, if we integrate the Wigner-Seitz ρ_x from $+L \rightarrow +\infty$, we find a total of one unit of exchange charge, in conformity with the usual interpretation that ρ_x represents the effect of the "fixed electron" not acting on "itself" in this Fermi-Dirac gas. However, the total Tomonaga exchange charge is zero, each term in ρ_x integrating to a magnitude of $1/2$. Until these discrepancies in the correlation expression in this special case are understood, no further development of the Tomonaga picture will be undertaken.

References

1. S. Tomonaga, Progress of Theoretical Physics 5, 544 (1950).
2. E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).

H. C. White